

The Journal of the SOCIETY OF DYERS AND COLOURISTS

Volume 69 Number 13

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THE SOCIETY OF DYERS AND COLOURISTS
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presidency of Mr. F. L. Goodall.

"THE SYMPOSIUM ON TEXTILE PRINTING"

After the toast of "Her Majesty the Queen", that of "The Symposium on Textile Printing" was proposed by—

Mr. ROGER M. LEE, who thought it might be of interest to give some account of the history of the industry and express views on some of the matters involved. It is unfortunately a fact that growing industrial success attracts so many to venture so far that ultimately the very success itself brings about conditions of a vastly different and less attractive kind.

In our own industry, developments abroad were bound ultimately to lead to a situation in which expansion had come to an end and we were compelled to reduce our scale of operations more closely in line with a constantly reducing demand. The real greatness of the industry has been thoroughly tried and tested during the period of readjustment,

of the Society

TEXTILE PRINTING

the Printing", at the Hotel Majestic, St. Anne's, December 1953. The attendance at the technical symposium of the Society and 30 visitors from

Symposium

December 1953, at 2 p.m.

President of the Society (Mr. F. L. GOODALL).

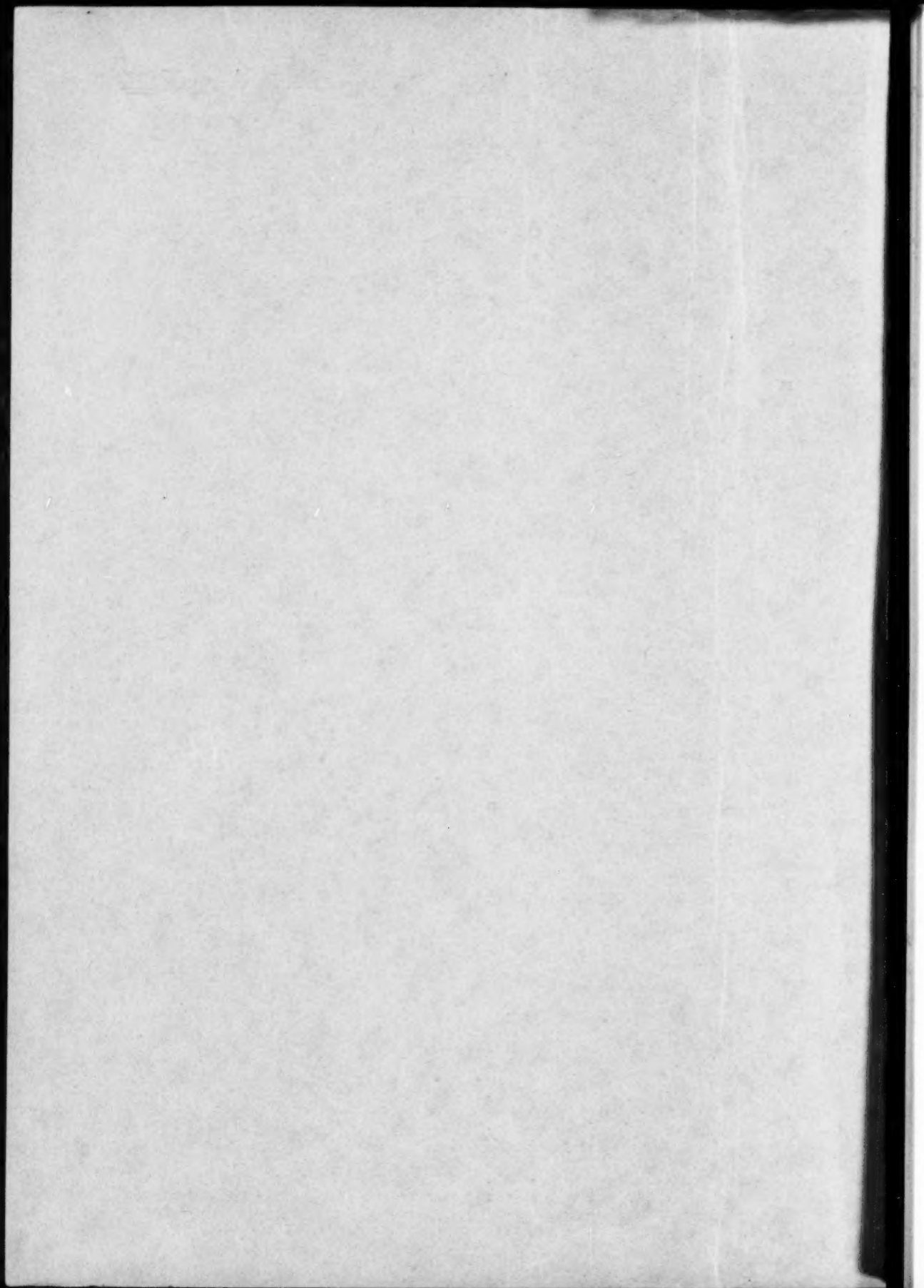
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Luncheon Dinner

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It was in fact 56 years ago, in 1897, that the industry received its first serious shock. The year previously there had been exported from this country over one thousand million yards of printed piece goods and in 1897 the figure was nearly 200 million yards less. It is true that the peak of activity had not been reached and was not reached until 1911, but 1897 may be regarded as the end of the period of expansion, to be followed by a short period, up to the beginning of the first world war, during which production fluctuated from year to year. This means that the majority of people in the industry to-day have worked through a period of redundancy, of constant and regular capacity to produce in excess of possible demand.

Behind the figures of reducing exports lies all the effort made to maintain what we can with the principal markets of the world. It often happens that when a market is disappearing, there is very much more effort put into this task of holding what we can than ever went into the development of the market originally. Alongside the decline of



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SYMPOSIUM ON TEXTILE PRINTING

The Society held its sixth symposium, on "Textile Printing", at the Hotel Majestic, St. Anne-on-the-Sea, on Wednesday-Friday, 23rd-25th September 1953. The attendance at the technical sessions was about 180-200, including some 80 non-members of the Society and 30 visitors from overseas.

Opening of the Symposium

Wednesday, 23rd September 1953, at 2 p.m.

The Symposium was formally opened by the President of the Society (Mr. F. L. GOODALL).

Mr. Goodall said that the Society was honoured by the presence of the President of the Schweizerische Verein der Chemiker-Coloristen (Dr. E. A. KRÄHENBÜHL) and the President of the Nederlandsche Vereniging voor Textielchemie (Ir. L. A. DRIESSEN). Dr. Krähenbühl represented also the International Federation of Associations of Textile Chemists and Colourists, while Svenska Färgeritekniska Förbundet was represented by Herr I. Norén, and the Verein der Textil-Chemiker and Coloristen by Dr. G. Schwen.

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The Symposium Dinner

The Society's Symposium Dinner and Dance was held on Friday, 25th September 1953, under the presidency of Mr. F. L. Goodall.

"THE SYMPOSIUM ON TEXTILE PRINTING"

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Mr. ROGER M. LEE, who thought it might be of interest to give some account of the history of the industry and express views on some of the matters involved. It is unfortunately a fact that growing industrial success attracts so many to venture so far that ultimately the very success itself brings about conditions of a vastly different and less attractive kind.

In our own industry, developments abroad were bound ultimately to lead to a situation in which expansion had come to an end and we were compelled to reduce our scale of operations more closely in line with a constantly reducing demand. The real greatness of the industry has been thoroughly tried and tested during the period of readjustment,

which has continued throughout the last fifty years.

It was in fact 56 years ago, in 1897, that the industry received its first serious shock. The year previously there had been exported from this country over one thousand million yards of printed piece goods and in 1897 the figure was nearly 200 million yards less. It is true that the peak of activity had not been reached and was not reached until 1911, but 1897 may be regarded as the end of the period of expansion, to be followed by a short period, up to the beginning of the first world war, during which production fluctuated from year to year. This means that the majority of people in the industry to-day have worked through a period of redundancy, of constant and regular capacity to produce in excess of possible demand.

Behind the figures of reducing exports lies all the effort made to maintain what we can with the principal markets of the world. It often happens that when a market is disappearing, there is very much more effort put into this task of holding what we can than ever went into the development of the market originally. Alongside the decline of

traditional markets is the effort to build up new ones where previously it had not seemed necessary to bring to bear all possible drive because of the comparative ease with which business in more prosperous markets could be obtained. As a selling problem, therefore, the industry, trading through the merchants and shippers, has had 50 years of very active though not always encouraging endeavour.

A further problem of redundancy is that of excessive plant capacity. It is obvious that plant capable of producing 1500 million yards in 1911 would be an embarrassment for an industry producing only one-third of that figure. The economist finds a ready answer to this problem by competition and the system of survival of the fittest but the fact is that many firms in our industry have been built up on the traditions of the family business and have refused to die or go under with anything like the ease that some of their competitors wished for.

No account, however brief, of this last 50 years of calico printing would be complete unless some reference is made to the human relations in the labour problem. Many of the workers in this industry are highly skilled craftsmen and behind these craftsmen have lain an even greater number of less skilled ancillary workers. Clearly it has not been possible to fight this rearguard action without very serious shocks to the people whose livelihoods depended on the industry's continued prosperity. Let there be no mistake about it, the problem has been much more serious than similar problems in other industries. Printworks requiring vast quantities of good clean water are usually situated in a country village and consequently a high percentage of the population is dependent on the works for its well being. The closure of one of these works can put a whole village out of employment and that is an added reason—and one much to their credit—why owners have been so persistent in their desire to keep going.

That is a very brief account of the background against which the industry has had to operate. It is an outline of circumstances but it is not in itself a measure of the skill and effort which have been put forward in order to keep the calico-printing industry as healthy as it is to-day. I would mention one or two of the things which have been done.

Back in 1897, with the first sign of a break in the industry's prosperity, there took place a number of financial mergers which resulted in something like 90% of the production capacity of the industry being under the control of three concerns. Mergers of this sort are never easy to negotiate, often they are not popular—I mustn't mention the word "monopoly"—but in our industry those that took place at the end of the last century did provide a solution to the problems of the time and they provided a financial pattern which was later to be followed throughout the economy of the United Kingdom.

After the first world war the cotton industry passed through a boom period and many of us can remember some of the less desirable developments

during that period. Later, they led to untold hardship during the slump which followed and the textile printing industry can be proud of the way in which it avoided any dangerous excesses in its financial affairs. Profits were high but dividends were moderate; there were few cases of re-floating and most concerns continued to live on their existing capital avoiding the failures which overtook other sections of the textile industry.

I must not give the impression that no closures took place. In fact, throughout most of this century, and especially during the late '20s and '30s, works were constantly being closed down and plant was being eliminated but the rearguard action was being fought in a reasonably orderly manner. Since the last war, redundancy has been dealt with in complete order, with retiring firms bought out by a common pool, subscribed to on an equitable basis by those who would remain to reap any benefits which might be expected to arise from the elimination of the surplus capacity.

This gives me an opportunity to make some reference to the Federation of Calico Printers. It has played a responsible part in the industry for many years and ready consultation has been possible between the managements of individual concerns. In passing I might also refer to the excellent relations which have always existed between management and the trades union organisations. The Federation of Calico Printers has undoubtedly been of material assistance in keeping at all times a balanced view of the major problems so that the interests of all parties have been borne in mind and I am firmly convinced that the actions taken by the Federation have been to the benefit of the textile industry, the operatives and the public.

I must admit to having spent most of my time this evening in speaking of the difficult times and the gradual recession which has been a feature of the calico-printing industry during the first half of this century. At the same time I do not want to leave the impression that we in the calico printing industry are filled with foreboding as to our future. There are many factors in our favour; our plant and equipment are up to date and in good repair and we claim to lead the world in technical knowledge. Extensive research work has been carried out in the industry: substantial economies have been made in engraving and in other directions and there has been constant development of newer, faster and brighter colours.

We shall require all the technical skill that we can muster because the production of special finishes, the processing of new fibres and many other things demanded by our customers to-day make the work of a calico printer entirely different from what it was in those old days of the huge shipping orders for the Eastern markets.

But, to succeed we shall require your assistance and in conclusion I would like to say a few words about the Society. I have taken the opportunity to do some research these last few days, and I would draw your attention to an article in the Jubilee issue of the Society's *Journal*

published in 1934, this article being written by Mr. George Hopkinson with the title *The Romance of the Society of Dyers and Colourists*. In it he quoted the opinion of Sir Henry Roscoe some few years after the Society's inauguration, regarding the value of "bringing men together and in drawing closer those bonds of friendship which should always prevail amongst the members with a community interest in the same objects." He went on to say: "In the past he feared many in the same trade or industry had fought shy of one another and did not want to come together."

This Symposium and those which have preceded it in the past few years are living evidence of the success of the Society in the fulfilment of the objectives indicated by Professor Roscoe, and all sections of textile finishing industry are appreciating more and more the part played by the Society in the scientific and technical development of their work.

To mention only two of the contributions made, there is first the *Colour Index*, which has proved its worth in all branches of colour industry in the past, and promises to be of even more universal use in its new edition, and secondly the work of the Fastness Committees, which has had international recognition, and in whose work we are glad to have been able to play an active part.

By its *Journal*, by section meetings, and by the longer and more comprehensive meetings like this one which are held from time to time, the Society continues to earn the thanks of all scientific and technical staffs in the dyeing and finishing industries.

So, Mr. President, with the help of your Society, it is my faith that in the years to come we shall continue to exercise all the initiative and enterprise which have been shown during the years of recession and, if this is done in the more stable conditions which we all hope lie ahead of us, who knows to what heights the industry may yet reach.

Mr. F. L. GOODALL (*President of the Society*), in responding to the toast, said: "The last time I addressed a gathering of the Society was some six weeks before the Coronation, when I said that the example of our charming Queen dedicating herself to a life of service should act to all men of goodwill as a call to renewed endeavour. Since then Her Majesty has passed through the rites of the Coronation in which we as a people have been privileged to share to a greater extent than ever before. I feel that having experienced that great and moving ceremony in Westminster Abbey we are in the mood to accept a call for endeavour and to fulfil it more than ever before. One of the ways in which as a Society we can respond to the call is by fulfilling the principal object of the Society which is the advancement of tinctorial technology. This phrase "advancement" is not perhaps the correct one since it may imply the advancement in a material sense of tinctorial technologists. Nothing is further from our ideals, and I believe that the best method of obtaining the advancement of technologists is by improving their technology. The improvement of technology, whether tinctorial or not, is a very pressing need in our international

life to-day, and as you are all aware has received government consideration and active promotion. Within the field of tinctorial technology this Society tries to improve the quality of its own field by a variety of means of which the oldest is its *Journal* and the most recent are perhaps the establishment of summer schools and symposia.

The present symposium is the sixth and has brought together a more representative collection of members of the Society and their friends interested in the technology of calico printing than has ever been the case before in this country. It has, I believe, been an undoubted success, due to the excellence of the papers presented, and the kindly and mostly disinterested criticism to which they have been subjected, supported by efficient staff work on the part of our Symposium Committee and the officials of the Society, but particularly because, as is usual with affairs conducted by this Society, of the atmosphere of mutual friendship and co-operation which always prevails in all its activities. We have been supported not only by the good wishes of many distinguished foreign societies but also by the presence and active participation of some of their most able members, and I hope that our foreign visitors will return to their homes feeling satisfied that if we cannot perhaps offer them all the hospitality which we should like, we can at least offer them our friendship and goodwill.

Mr. Lee has referred in passing to the importance of human relationships which I regard as a vitally important part of any individual or society's activities. There are no degrees or qualifications obtainable at any university in human relationships, and each one of us must work the problem out for himself according to his own innate qualities and ideals. As a Society we have reached a certain position in this, our seventieth year of existence, by virtue of co-operation and goodwill between our members. That spirit of co-operation and goodwill amongst ourselves is already extended to other societies of similar ideals and interests to ourselves.

We are already co-operating actively with the A.A.T.C.C. in the production of the Second Edition of the *Colour Index*, and we have the most cordial relations with other societies of our own type throughout the world, but we have now to seek the active assistance of some other societies not directly concerned with dyes and textiles, in the furtherance of the advancement of tinctorial technology, by another new project of the Society which is almost completed and of which I am privileged tonight to make the first announcement. This is the establishment by this Society of a system of qualification by examination of individuals to denote their ability to practise tinctorial technology. I use the word "practise" advisedly because one of the points on which the Council of the Society and its Diploma Committee have been insistent from the inception is that any qualification granted by the Society should be obtainable only by a period of practical experience in tinctorial technology in addition to an adequate knowledge of the fundamental pure sciences and a particular aspect of tinctorial technology. The Society believes that there has been a real need for such a qualification which would be

accepted in industry as something of real worth and considers that in providing it it is only fulfilling its objects.

Since tinctorial technology covers the whole art and science of colouring almost anything, it is obvious that if we are to succeed in our aims we must have the help of some other bodies with a more detailed knowledge of certain materials to be

coloured than we ourselves possess. The scheme for the award of diplomas is complete except for a few minor details, and it is hoped to make a detailed announcement towards the end of October. In the meantime the societies whose active assistance we need have all been approached and in the majority of cases have indicated their willingness to collaborate with us."

The Production of Printing Rollers by Electrodeposition

E. A. OLLARD

The process and the plant for depositing printing rollers are described in detail, and also the process employed for facing rollers with chromium.

Requirements for Printing Rollers

A printing roller is normally produced from copper, and it is essential that the metal should be homogeneous and free from pores, inclusions, or other imperfections which would cause difficulty in etching. Also, the roller is likely to be used a number of times, which means that it must be capable of being built up, after use, to its original diameter. The surface must be extremely smooth and highly polished, and the metal must be capable of withstanding a certain amount of pressure without distortion.

The most convenient way of producing a suitable roller to fulfil these conditions is by electro-deposition. Normally a steel tube is used as the base of the roller, and this is mounted on suitable end plates on a spindle. The whole is then copper-plated, a thick deposit of copper of suitable mechanical properties being produced on the outer diameter. This is then turned to the required size and polished, after which the design is etched on it. The roller may then be used directly or, if it is required for a long run, it may be faced with a hard metal such as chromium.

After completion of the run, the facing metal is stripped, and the cylinder turned down and again built up by electro-deposition.

In some cases it is found more convenient to deposit on the cylinder a thin non-adherent layer of copper which requires little or no mechanical finishing and which can be stripped off after use.

Cylinders for different purposes vary very considerably in size, and the actual process used and the method of production will depend largely on the size of the cylinder, the number of cylinders required per week, and the general production facilities.

Methods of Production

The original cylinder, normally consisting of a steel tube, will be provided with some method of mounting on to a central spindle. Since for most purposes it is preferred to use an acid copper solution for plating the copper deposit, and this solution cannot be used to plate steel directly, it is necessary first to copper- or nickel-plate the steel tube.

The tube will generally have a machined surface, and therefore will not need a great deal of pickling, but will require to be carefully cleaned in a standard type of alkaline cleaner. It should then be given a dip in 10% sulphuric acid, followed by scouring with a brush and some pumice powder. After this, it should be given a second dip in acid, carefully swilled, and immersed in the plating tank.

Nickel is, perhaps, preferable to copper for plating the cylinder, as it forms a good base for the

acid copper deposit, but many plants may not have a nickel vat available. If it is decided to use nickel, a standard nickel solution containing 3 lb. of nickel sulphate and 4 oz. each of nickel chloride and boric acid per gallon will be suitable. The cylinder may be completely immersed in this solution, or it can be rotated on its spindle, but it is advisable to plate the inside of the cylinder, so that any acid copper solution which finds its way inside the cylinder during the deposition process will not attack the cylinder and cause trouble; or the inside may be protected with a suitable lacquer. The end plates and any other parts of the cylinder which are likely to come in contact with the solution during deposition should also be plated.

Alternatively, the steel parts may be plated directly with copper in a copper cyanide solution. Any standard type of copper cyanide solution can be used for this purpose.

After the steel parts have been plated with nickel or copper, the whole cylinder is assembled, and a thick layer of copper deposited in an acid copper solution. This is normally chosen because it is the most convenient solution available to give a heavy deposit of copper of the required mechanical properties. In some cases other solutions have been put forward and certain claims made for their use, but it seems doubtful whether any of these will become popular. The cyanide cannot be worked at the same high speed and, although it gives a more finely crystalline deposit, it is more difficult to control; also, the highly poisonous nature of the solution makes it somewhat more unpleasant to handle. Some claims have lately been made for a copper fluoborate solution, but at the present, so far as the author is aware, this solution has not been used on a production basis for this type of roller. It is proposed in this paper, therefore, to deal only with the standard acid copper solution.

Two different methods of arranging the cylinder for deposition are in general use—

(a) The cylinder is arranged horizontally about one-third below and two-thirds above the solution level.

(b) The cylinder is arranged vertically and totally immersed.

In each case the cylinder is rotated during deposition.

The choice between these methods will depend on the size and shape of the cylinders in question, the available plant, and, to a certain extent, the personal preference of the operator. Both methods have been used satisfactorily and both have claimed advantages. In making a choice, the

following factors may be taken into consideration—

A—HORIZONTAL ARRANGEMENT

Advantages

- (i) The size of the vat required is relatively small, i.e. the cylinder can be treated in a long shallow vat.
- (ii) The rotating gear is quite simple; the spindle is above solution level, and can be rotated with a pulley and belt.
- (iii) It is possible to watch the surface of the cylinder during deposition, and to remove any material which lodges on it and which otherwise might produce a nodule. In some cases it may be desirable to run a burnisher or brush continually over the surface.
- (iv) Since the surface of the cylinder comes out of the solution and re-enters it during rotation, there is a certain amount of wash, which tends to remove suspended matter and bubbles.

Disadvantages

- (i) Only one-third of the cylinder is under the solution at any time, and therefore the maximum rate of deposition is reduced.
- (ii) The cylinder cannot be rotated at a very high speed, because if this were done it would send up a spray of solution, and this again limits the speed of deposition.

B—VERTICAL SUSPENSION

Advantages

- (i) Owing to the fact that the cylinder is totally immersed and can be rotated at a high speed, it is possible to use very high current densities and to obtain a hard, close-grained copper deposit.

Disadvantages

- (i) The plant required is somewhat more complicated, particularly for larger rollers.
- (ii) One cannot watch the surface during deposition, and there is a greater danger of suspended matter, etc. producing nodules.
- (iii) If it is desired to burnish or brush the surface during deposition, the necessary mechanical gear is more complicated.
- (iv) There may be a slight difference in thickness and possibly structure of the copper from one end of the cylinder to the other.

The choice between the two methods, therefore, will have to be made after all the above facts have been taken into consideration. Both methods are in use, and both methods can produce satisfactory printing cylinders.

Acid Copper Solution

The standard acid copper solution consists of 2 lb. of copper sulphate and $\frac{1}{2}$ lb. of sulphuric acid per gallon. This solution would appear to be very simple to produce and operate, and, in fact, such a solution will always deposit copper of a kind. When, however, it is required to deposit pore- and inclusion-free copper of standard mechanical properties suitable for etching, it is necessary to take very great precautions in both the preparation

and the use of the solution, otherwise trouble will be experienced.

The basic composition of the solution is not of great importance, and a variation of 10% or more in the concentration of the copper sulphate or sulphuric acid will make very little difference to its performance. Unfortunately, however, very small traces of impurities in the solution will considerably modify the crystalline structure of the copper. This is particularly true of organic matter. For example, one part of glue or gelatin in 10,000 will make a very considerable difference to the properties of the copper being deposited. The successful working of this solution, therefore, will depend principally on prevention of contamination and on constant purification so as to keep the deposit to the required properties.

This solution is used with soluble copper anodes, which contain a small amount of metallic impurities. Only high-quality anodes of electrolytic copper should be used. They will, however, contain normally a small amount of iron together with traces of some of the other commoner metals. Even when the anode is relatively free from other impurities, it may still cause trouble in the plating solution if it does not dissolve evenly. Many samples of copper whose composition from the chemical point of view is suitable dissolve under the conditions of the plating vat to give a fine sludge of copper or copper oxide particles. These particles, if sufficiently fine, will remain suspended in the plating solution, and ultimately may be carried to the growing surface of the roller, where they may lodge, forming a nodule.

To obviate this trouble it is desirable to make sure in the first place that the anode has been suitably rolled and heat-treated so that it will dissolve as evenly as possible. It is then normally found beneficial to enclose the anodes in a bag made of Terylene (ICI) or polyvinyl chloride fabric. It is also necessary to arrange constant filtration of the solution, which is circulated by means of a suitable pump from the plating vat through a filter. In some cases an individual pump and filter are arranged on each vat, while in others the solution is allowed to overflow from the plating vat into a sump tank, from which it is pumped to a head tank and then allowed to flow back from this to the plating vat by gravity.

By suitably bagging the anodes and by means of constant filtration, it is possible to maintain the solution reasonably free from suspended matter. It is still, however, necessary to exclude the various impurities which are likely to affect the process. Normally the solution will contain a small proportion of iron and other metallic impurities, and since they tend to work out slowly during the deposition process, trouble is not usually experienced from them.

The main troubles of the process are normally caused by organic material, to which this solution is extremely susceptible. These may come from the following places—

- (i) The materials of which the plant is constructed. For example, some types of rubber linings of tanks contain accelerators or impurities

which will slowly leach out and cause trouble in the solution. Resin from wood and materials from stopping-off varnishes, etc. are also liable to cause trouble.

(ii) Many samples of copper sulphate may be found to be contaminated by small traces of wood and resinous material from the packing, etc., and this may cause difficulty when the solution is first made up or when additional copper salts are added to it.

(iii) The water used for making the solution may contain small quantities of organic matter or chloride, which is also detrimental in quantity. Since this water is being continually added to replace evaporation, any impurities in it are likely to accumulate.

(iv) The solution may become accidentally contaminated owing to human error; for example, someone may drop a piece of emery cloth containing glue, or a screwdriver, into the solution.

(v) Trouble may be caused by extraction of such material as three-ply wood used to cover the tank when not in use, or by drips due to condensation on the ceiling of the shop.

Even when all precautions have been taken to exclude impurities, however, there is the probability that from time to time a certain amount of contamination will occur, and this will have to be dealt with. As previously mentioned, metallic impurities will gradually work out of the solution with use, but it may be necessary to adopt special methods for removing organic matter.

The most convenient method for doing this is to treat the solution with activated carbon. This may be done in several ways. If a solution is badly contaminated, the powdered material may be added directly to the plating vat, stirred up, and allowed to settle; then the solution is filtered off, and the vat cleaned out. In the case of mild contamination, the activated carbon may be used in the filter, or alternatively the solution may be circulated through a tower containing carbon granules. Activated carbon will take out a considerable amount of organic material, though it will not deal with every type of impurity which may cause trouble, and in some cases it may be necessary either to oxidise or to reduce the solution to break down the materials concerned. In many cases an oxidising treatment followed by activated carbon will give the required result. The solution may be oxidised chemically by the addition to it of such substances as hydrogen peroxide or potassium permanganate or, in some cases, the oxidation can be carried out electrolytically by running the solution with a lead anode.

It is always advisable to treat freshly made-up solution for any removable organic material before use, and then to run it for at least 24 hr. on pieces of scrap metal before trying to deposit on to a cylinder.

Activated carbon will take up about one-third of its weight of organic matter, generally absorbing the large molecules first. A number of different grades are available, some being more suitable than others.

In the making-up of the solution, only high-quality chemicals should be used. The sulphuric acid used must be free from arsenic and should be of pure commercial quality (R.O.V.). The solution should be prepared with either distilled water, or demineralised water produced by an ion-exchange plant. The water used should be free from suspended matter, chlorides, calcium salts, and organic impurities. The copper sulphate is first dissolved by heating the water in a boiler or other suitable vessel, and adding the copper sulphate crystals. The solution is then transferred to a plating vat, preferably through a filter. The sulphuric acid is then added, and a final check is made on the composition of the solution by analysis.

Plant

The plant required will consist of the following—

1. Electrical installation to provide the low-voltage direct current
2. Plating vats
3. A circulating and filtration system
4. Apparatus for handling and rotating the cylinder during deposition
5. Arrangements for heating the solution.

1. ELECTRICAL PLANT

Copper deposition requires a low-voltage direct current. Generally the voltage required on a tank for depositing cylinders will be of the order of 4 volts, though this may vary considerably according to the current density and the solution used.

In a solution of this type the current density may vary considerably. Generally speaking, it is desirable to use as high a current density as convenient, but this requires heavy conductors, satisfactory methods of conducting the current into the cylinder, and also high speeds of rotation. Current densities of 100–200 amp./sq.ft., therefore, may be found to be convenient for most purposes, and it is possible that in many plants it will not be economic to exceed this figure. Where, however, the time of deposition is a controlling factor, current densities up to 1000 amp./sq.ft. can be used when satisfactory precautions are taken. Low-voltage direct current may be obtained either by means of a special low-voltage D.C. generator directly coupled to an electrical motor or by means of a metal rectifier. This latter piece of apparatus has the advantage that it has no moving parts and therefore requires little or no maintenance. It can be made to function directly from a three-phase A.C. main and it can also be provided with a regulator so that the current through the vat can be adjusted. The rectifier or generator should be located near the plating tank, but preferably in a separate room, so that it does not come in contact with the plating shop fumes. The size of the installation will depend on the size and number of cylinders to be deposited and the current density used. In some plants a large generator or rectifier is used to feed the whole shop, but it is generally preferred to arrange a separate unit on each vat, as this simplifies the control and has the advantage that the efficiency of the apparatus may still be

maintained when the shop is not fully loaded. Connections to the vat are made with copper bar, it being usual to allow 1 sq.in. of cross-section per 1000 amp. A voltmeter and an ammeter should be provided for each vat.

A suitable method of contacting on to the roller will be required. This normally takes the form of a copper drum on the roller shaft on which a copper brush rubs. In the case of small cylinders sufficient contact may be made through the bearing.

2. PLATING VAT

The vat must obviously be constructed of some material which will not be attacked by the solution. Originally wooden vats lined with sheet lead were used, but at the present time vats are constructed of mild steel and lined with rubber, polythene, or polyvinyl chloride. In some cases vats are built of cement and lined with asphalt, but these have the disadvantage that they cannot be moved.

As previously mentioned, it is important to make certain that the lining of the tank will not contaminate the solution. From this point of view a polythene lining is preferable, but polythene is a difficult material to apply satisfactorily to a tank of any size because one cannot get a satisfactory bond on to the tank, and the difference in coefficients of expansion tends to make the polythene pull away from the tank and crack. Hard rubber is normally satisfactory, and so are certain qualities of semi-hard rubber, but tanks required for this purpose should be obtained from reputable suppliers who have experience of this work, as some types of rubber are found to contaminate the solution. Plasticised polyvinyl chloride is unsuitable, but the hard laminated type may be satisfactory, though sufficient information on this subject is not yet to hand. Lead lining can be used, but has the disadvantage that it is conducting and tends to produce various stray currents. It is usual, therefore, to insulate the sides of the tank with glass sheet.

The design of the tank will depend on the size of the cylinder to be deposited and the method by which it is to be handled. The tank will need to be provided with an overflow for the circulation of the solution. In some cases, also, a drain may be provided in the bottom for emptying. Some type of framework will be required round the top of the tank to support the anode bars and also to carry the rotating gear for the cylinder. This can be fixed to the tank or can be made separate as desired.

3. PUMPS AND FILTERS

Acid copper solution is a difficult material to handle, and the piping, pumps, and filters used must be specially constructed for this purpose. Normally the material may be handled in either rubber, rubber-lined, lead, or polythene pipes. Sump or head tanks, if used, should be of the same general type as the plating vat.

Several types of pump can be used, but it is, of course, essential that the pump shall be constructed, or at least lined, of some material which is not attacked by the solution. Pumps lined with hard rubber can be obtained or, in certain cases, they

can be made from stainless steel or silicon-iron. Diaphragm and rotary pumps are both used for this purpose. In some smaller plants air lifts are used, but these are not very suitable to work in conjunction with a modern type of filter.

For filtration a filter press is suitable if used in conjunction with a suitable fabric. A number of other types of filter mostly employ a filter aid such as kieselguhr.

It is not proposed to deal at great length with pumps and filters here, as these have been dealt with elsewhere¹. In choosing a pump and a filter it is necessary to make certain that these will handle the required quantity of solution. Manufacturers are often somewhat optimistic about the amounts handled by their apparatus. This applies particularly to the filtration plant. If too small a filter is used, it will tend to load up too quickly and require constant attention. It is therefore preferable to employ a filter on the large side, as this will considerably reduce maintenance costs.

For the best results the pump and the filter should at least be capable of turning over the entire volume of the plating tank in some three hours. Where very high current densities are being employed, it may be desirable to reduce this period to two hours or less.

4. HANDLING AND ROTATING GEAR

Since the majority of cylinders are too heavy to be lifted conveniently by hand, it is necessary to have some method by which they can be manipulated. Normally the cylinders are placed on specially designed trucks to move them from one department to another. Generally, preliminary cleaning of the cylinder is done on this truck, the cylinder being rotated by hand and a tray arranged underneath it to catch the solution used. The cylinders are most conveniently handled by means of an electric block running on an overhead rail arranged above the tanks, so that they can be picked up from trucks and lowered into the deposition tanks. In certain cases, however, where, because of the low headroom or for some other reason, such an arrangement cannot be employed, specially designed trucks are used embodying a lifting gear which is arranged to lower the cylinder into position in the vat.

If the cylinder is being deposited in a horizontal position, it is arranged so that the spindle lies in two half-bearings at either end of the tank. The spindle being just above the level of the solution, this does not present any great difficulty. It is usual to cut away a piece of the end of the tank to allow the spindle to be lowered below the tank level, since otherwise it is necessary to have the solution very near the top level of the tank itself, and this is liable to increase splashing, etc.

When the cylinder has been lowered into position, it is connected by means of a belt to the rotating gear, and a brush is arranged to carry the current to it. The rotation of the cylinder should be started as soon as possible after it is lowered into the tank, and if there is likely to be any delay it may be advisable to keep it turning slowly so that its surface does not dry. As soon as it is connected up,

the rotation is started and then the current is applied. It is generally preferred to start for a few minutes at a lower current and then gradually to increase it to the required value. The time taken will, of course, depend on the thickness of copper required and the current density, and this can be calculated by means of standard tables. The end plates and any part of the spindle likely to come into contact or be splashed by the solution are generally stopped off by means of a suitable lacquer or paint. Such materials can be obtained from the suppliers of the plant. This prevents corrosion, and also the deposition of copper on parts on which it is not required.

In the case of cylinders which are to be deposited vertically, the same general arrangement applies, but the cylinder is, of course, suspended by one end only, and the whole plant requires considerably more headroom. Where large cylinders are to be dealt with, it may be found desirable to sink the vat into the floor. The top of the vat, however, must not be less than 3 ft. above floor level. For large cylinders it will usually be desirable to have a bearing at the bottom of the tank, but smaller cylinders can be arranged so that all the bearings are above solution level and the cylinder projects into the solution. The cylinder may be rotated by means of a belt and pulley, or by any other suitable method.

In some cases arrangements are made to rub the surface of the cylinder during deposition with an agate burnisher or other suitable instrument. This burnisher is arranged to work to and fro automatically over the whole length of the cylinder. This process was very popular at one time, it being claimed that it gave a hard close-grained deposit, but it is somewhat doubtful whether the results justify the added cost of the plant, etc., and quite satisfactory cylinders can be deposited without its use.

5. HEATING THE SOLUTION

Heating of the solution may be accomplished either in the plating tank itself or in some part of the circulating system. Where steam is available, this is a convenient method of heating, and lead or lead-covered coils may be employed. Alternatively, a heat exchanger made of graphite or some suitable inert material can be used. If steam is not available, electrical immersion heaters can be substituted. These must obviously be constructed of material not attacked by the solution. Heaters having fused silica jackets will be found convenient.

Whatever temperature is used, this should be controlled as closely as possible, preferably to $\pm 2^\circ$ or 3°F . This may be done manually or by means of a thermoregulator.

Deposition Conditions

In order to obtain a satisfactory copper deposit for the purpose required, it will be necessary to control the following conditions—

1. Composition of solution
2. Freedom from impurities
3. Temperature
4. Current density

5. Speed of rotation
6. Addition agent if used.

1. COMPOSITION OF SOLUTION

The composition of the solution may be controlled by analysis. For shop tests, however, a hydrometer may be used and the solution kept at constant density. To check the composition it will then be necessary to determine the amount of acid present. This may be done by titrating the solution with standard alkali against methyl red as indicator or by estimating the amount of acid present from the conductivity. The conductivity may be measured by means of a standard apparatus, but a good idea of whether this is varying can often be obtained by a reading from the voltmeter or ammeter. If it is noticed that a higher voltage than usual is necessary to maintain the desired current, and the temperature, anode area, and density of the solution are correct, then it may normally be taken that the solution is low in acid.

2. IMPURITY CONTENT

Since very small quantities of organic material will affect the deposit, it is quite impossible to control this by any type of analytical procedure. As previously mentioned, every precaution should be taken to exclude or remove impurities. If, after this is done, the copper is found to be hard, brittle, rough, or otherwise unsuitable, then contamination of the solution should be suspected, and a purification treatment employed.

3. TEMPERATURE

The optimum temperature will vary slightly with different plants. Normally, raising the temperature will enable higher current densities and therefore shorter times to be used. If the current density remains constant, an increase in temperature will produce a somewhat softer deposit. The temperature of deposition, however, is generally limited to about $110\text{--}120^\circ\text{F}$. Above this temperature, one obtains excessive evaporation, and also any rubber parts used in the construction of the plant may be softened and cause trouble. In some cases the process is worked at room temperature, which obviates the difficulty and the cost of heating. This, however, will increase the time taken, and it is generally preferred to warm the solution to somewhere between 80° and 100°F . If the solution temperature is allowed to fall below 60°F ., trouble may be experienced with the anodes, and in some cases it may be found quite impossible to get any current through the system at all until the anodes have been removed and scrubbed.

4. CURRENT DENSITY

The optimum current density will have to be found for the particular plant in question. This will depend on the thickness of copper required and the time allowable for the operation. It is obviously useless to increase the size of the electrical plant, rate of filtration, etc. to save a few hours of deposition time if this entails the cylinder being removed from the tank in the middle of the night and waiting until the next morning to be machined.

In most plants a definite routine is arranged, and the current densities are chosen so that the deposition will be completed at the required time. Normally, increasing the current density will tend slightly to produce a finer, harder structure, but over the range used will not have very much effect. Various automatic devices can be obtained for controlling current, and, particularly if the process is carried out largely at night, it may be found desirable to employ such, or at least to use recording instruments so that a record may be kept.

5. SPEED OF ROTATION

The higher the speed of rotation the higher the current density that can be used, but the optimum speed will normally be controlled by convenience. If a high speed is used, a considerable amount of splashing will be experienced and the power required for rotation will be increased. Normally, therefore, a cylinder is rotated just fast enough to carry with it a thin layer of solution. If the cylinder is partly immersed, it must never turn so slowly that the surface becomes dry. Increase in speed of rotation will have the same general effects on the structure as an increase in temperature or a reduction in current density.

6. ADDITION AGENTS, IF ANY

The general structure and the mechanical properties of a copper deposit can be very materially modified by quite small quantities of certain materials, generally called "addition agents", added to the plating solution. A number of substances have been used for this purpose, and include such materials as glue, sugar, arsenic, casein, corn syrup, and certain special organic chemicals. The principal difficulty in the use of these materials is that they are difficult to control, and are inclined after a time to produce undesirable results. Also, it may be found that when such materials are used the deposit produced does not etch in the standard manner, which may produce difficulties during the etching process.

One of the most satisfactory addition agents for an acid copper solution is phenolsulphonic acid. This substance, when added to a copper solution in the correct quantity, will produce a harder, more finely grained deposit, but again this deposit may not etch in the normal manner and care should be taken in the use of the material.

The best method of making an addition is to take 0.5 g. of pure phenol crystals per litre, and add to this an equal weight of concentrated sulphuric acid. The mixture is then heated to 100–110°C. for 1 hr. It is allowed to cool somewhat, and then added to the plating solution. The solution must subsequently be worked for about two days, after which it will turn a greenish colour, and the copper will become finer-grained and harder.

General Control of the Process

If the above precautions are carefully observed, the deposit obtained should be smooth and regular, and should machine and etch accordingly. However, it is desirable to keep a very careful check on the cylinders as they are machined and etched to make certain that the deposit is up to a satisfactory

standard. If the cylinders show any sign of roughness or porosity, or if the copper does not machine properly when put on the lathe, then the deposition process should be immediately overhauled to make certain that all the conditions are being carefully maintained.

Assuming the cylinder to be machined and etched correctly, the only other difficulty to be experienced is excessive wear during use. While the copper deposit is usually blamed for this trouble, it is by no means always the primary cause, and sometimes excessive wear is due to faults in the machine. However, the hardness of the deposited copper can vary very considerably, and if the deposit is soft it may tend to distort even if covered with a hard layer of chromium or other metal. It is possible to obtain a direct hardness value on the deposit by means of a micro-hardness test, but this, of course, requires special apparatus. Where, however, trouble is experienced, it may be advisable to have the deposit tested for hardness to estimate definitely whether this is the cause of the trouble. Should the deposit be soft, its hardness may be increased by increasing current density, reducing temperature, or increasing the sulphuric acid content of the bath. All these changes will tend to increase the hardness, but if a large increase in hardness is desired, then it will generally be necessary to use an addition agent such as phenolsulphonic acid.

In certain cases the copper may appear to be brittle, and instead of machining normally will tend to chip off the roller and give a rather roughish surface. This trouble is usually caused by organic contamination of the solution, which should be carefully treated with activated carbon.

Use of Thin, Strippable Layer of Copper

In the process described above it is presumed that the cylinder will be built up with a copper deposit, machined, and etched, and then after use turned down and again built up to size.

This, of course, entails two machining operations, which are expensive. To overcome this difficulty and reduce costs, a process has been used depending on the deposition of a thin layer of copper, on which the design can be etched and which can be removed by stripping from the cylinder after use.

For this purpose the cylinder must be machined to just below the finished size to allow for the thickness of the deposited copper. It is then prepared for a non-adhesive deposit by treatment with a special solution which forms a film on the metal surface, preventing adhesion of the deposited copper. A number of these solutions have been used, their nature depending on the metal on which the deposit is to be made. If a nickel surface is used, this may be treated with a solution of potassium dichromate (2 oz./gal.), which will slightly oxidise the surface. On a copper surface one of the most satisfactory is selenium nitrate, which will form a thin layer of metallic selenium on the surface. A dilute solution of sodium sulphide also, however, will prevent adhesion without interfering with the deposition of the copper. When depositing on a filmed surface, care

should be taken to see that the roller does not remain in the plating solution for any time without current passing, as this will remove the film and the deposit will not strip.

Since a comparatively thin layer of deposited copper is all that is required, this layer can be deposited smooth and even, so that it does not require machining, all that is necessary being to give a light polish. After use it can be cut through and stripped away from the roller, which is then ready to receive a new deposit.

Facing of Cylinders

Where only short runs are required, the etched copper cylinder can be used directly for printing. Copper, however, is a comparatively soft metal, and such a cylinder will not stand up long in the average printing machine. Where long runs are required, therefore, it is desirable to face the etched cylinder with some harder metal.

Nickel, iron, and chromium have been used for this purpose. Nickel can easily be deposited, but has the disadvantage that it is difficult to remove it again without etching the copper. Iron can be easily removed, but it is not easy to deposit a satisfactory coating, and the coating is liable to rust or corrode from other causes. Chromium, therefore, is usually preferred for this purpose, because it can be deposited easily in a thin, bright, even coating; it is resistant to most of the substances with which it is likely to come into contact; it has an extremely hard surface and resists abrasion well; and it can be easily removed without material attack on the underlying copper surface.

To face a cylinder with chromium, the polished and etched cylinder is very carefully cleaned, usually by careful brushing with an alkaline solution containing a cyanide and some precipitated chalk. Then, after being swilled, the cylinder is lowered into a chromium-plating vat.

The cylinder may be plated horizontally or vertically, a similar apparatus being used to that for plating copper, but the chromium-plating tank normally being constructed of steel, lined with antimonial lead sheet, and provided with exhaust ducts down the sides to remove the fumes and spray produced by the process.

The solution employed is usually a normal chromium-plating solution containing 250 g. of chromic acid and 2.5 g. of sulphuric acid per litre. Some people, however, prefer to use a rather more concentrated bath, the two ingredients having the same ratio. The solution is worked warm, normally at about 90–100°F., and a minimum current density of about 100 amp./sq.ft. is required, otherwise no deposit will be obtained. If the process is carried out with the cylinder in the horizontal position, great care must be taken not to allow the cylinder to remain stationary in the plating solution between the time when it is entered and the time when deposition begins, since the chromic acid solution will attack the copper at the water-line and produce a mark.

Fine sprays of chromic acid are injurious to health, and the facing plant must be provided with adequate exhaust arrangements. In the horizontal

type of plant it is usual to arrange a hood to go right over the cylinder while it is being deposited. If the cylinder is being deposited vertically, it is not essential to rotate it, as it can be arranged with a circular anode, so that all parts obtain an even deposit. For large cylinders, however, the vertical arrangement means a large tank and a somewhat more difficult procedure for entering the cylinder.

If this process is carried out carefully, a bright, even deposit of chromium will be obtained over the whole surface. Quite thin deposits will prolong the life of the cylinder very considerably, and normally a deposit of 0.0001–0.0002 in. will be found sufficient, though thicker deposits may be desirable for some purposes. Where comparatively thick deposits are required, it may be found that the chromium tends to build up slightly at the ends of the cylinder, but this can usually be avoided by screening or some other suitable method.

Lead anodes are used for this process, and during working should become covered with a brownish film of lead dioxide. The chromium is taken entirely from the solution, and therefore additions of chromic acid will be required from time to time to maintain its metal content. The bath must be kept at constant density, but periodically it will be necessary to check the sulphate content by analysis and adjust this to the correct ratio of 1% of the chromic acid content.

This process is not difficult to operate, but the conditions of temperature and current density are usually critical. The temperature must be regulated to within $\pm 2^\circ\text{F}$. It is also essential to control current density within close limits after the optimum current for each type of cylinder has been found by experiment. If this is done, satisfactory deposits should be obtained, but on working the solution it may be found, after a period, that a rather higher voltage is required to maintain the required current density. This is due to the fact that a certain amount of trivalent chromium compounds form in the solution and reduce its conductance. If the content of these compounds rises, it may be necessary to oxidise them by working the solution with either a porous pot or a number of small pieces of steel rod for a cathode instead of the roller. Care should be taken to see that the anodes are kept clean and are covered with a brownish dioxide film. If they become covered with a yellow chromate film, it is liable to aggravate the above trouble.

After deposition of the chromium, the cylinder should be ready for service, but it may be necessary to give it a slight final polish, which can be done if desired with a soft mop of suitable composition.

After the cylinder has been in service for some time, it may be found that the chromium deposit shows signs of wear. The chromium can then be removed by solution in dilute hydrochloric acid and a fresh deposit applied without disturbing the design. This enables the life of the cylinder to be prolonged several times.

Chromium has not only a high hardness but also a low coefficient of friction against steel. This reduces the wear of the doctor blade on the

cylinder. It also reduces corrosion by the majority of printing inks and cleaning fluids which are used.

Troubles likely to be experienced

From time to time under industrial conditions it is found that a number of small troubles will be experienced with printing cylinders, and it is usually difficult to determine their exact cause or even the part of the process that is at fault. It is, however, very desirable to establish the cause as soon as possible, so that the necessary action may be taken.

Troubles may arise from faults at the following stages—

- (1) The initial deposition of copper
- (2) The machining and grinding process
- (3) The etching process
- (4) The facing process
- (5) On the machine.

It is sometimes difficult to determine exactly which of these processes is at fault, it being usually found that each of the people concerned will blame the other processors for the trouble. Thus the fact that the deposit machines or etches badly may be due to the deposition conditions, and it is not always easy to establish whether this is so. Excessive wear on the cylinder is usually blamed either on the initial deposit or on the facing process, although it may be due to a fault on the machine. When troubles occur, it is necessary to make a very careful examination and try to determine what factors could have caused the observed defect. Each of these will then have to be carefully checked.

For example, it may be found that the cylinders are not giving the desired life. This may be due to incorrect setting of the machine, but it is quite probably due either to the initial deposit being too soft or to the facing being too thin. Careful examination of the working cylinder will very often show the cause. If the copper deposit is soft, some distortion will have taken place around the edges of the etched design. The thickness of the facing material and the hardness of the surface can be determined. If all these are found to be correct, then there is a strong presumption that the printing machine itself is at fault, but if the cylinder shows distortion of the copper and the chromium is found to be thin, then the deposition processes should be overhauled.

Faults in the deposition of the copper which produce hard, brittle metal or non-homogeneous material are easy to recognise, but in some places complaints may be received from the etching department that the copper cylinders do not etch correctly. This, of course, may be and often is due to the etching process itself, but it must be remembered also that a change in the crystal structure of the copper will affect the etching process. This may be checked by examining a section of the deposit under the microscope and comparing it with a section of a deposit which behaved normally.

Bimetal Printing Surfaces

From time to time processes have been evolved for using bimetal printing plates, working by a somewhat similar method to a lithographic process. A number of these plates have been used successfully from time to time on half-tone work, but, so far as the author is aware, this type of process has not been applied to printing rollers, since the rollers are normally used for photogravure. It is possible, however, that some of these processes could be adapted to continuous printing by use of cylinders, and it is therefore felt that a brief note on these types of processes is not out of place in this paper.

Basically, the processes involve the plating of a copper or other metallic surface with a facing of another metal, e.g. chromium. The resist is then applied, and the facing metal is etched through to the underlying plate. One of the metals is then treated so that it will not take the ink; for example, the copper may be amalgamated with mercury, or the chromium treated with some material that will make it take a film of water. The surface is then inked over, the ink remaining on the untreated metal and being wiped away from the treated part.

These processes have the advantage that they simplify the etching procedure, since the depth of the etch is regulated by the thickness of the facing metal. Some of these processes have been worked with satisfactory results on plates, but it is rather doubtful whether they would show any advantage when compared with the normal type of gravure process. For some purposes, however, they might be applied.

* * *

The above description covers the production of printing cylinders by electrodeposition. In carrying out this process, it must be remembered that, while it is comparatively easy to deposit a copper cylinder, great care and attention to detail must be exercised if the plant is to make, on a production basis, cylinders which will satisfactorily withstand long runs.

In the setting up of the plant, some thought must be given to the most convenient method of depositing the cylinders, and also to whether they shall be deposited solid, and turned down and rebuilt after each operation, or whether a non-adhesive layer shall be applied which can be removed by stripping. No general guidance can be given on these matters, as the process must be chosen after consideration of the size of the cylinders concerned, the number required, and the length of runs. Only after careful consideration of all these points is it possible to come to a decision as to the best method to use. Broadly speaking, all the methods described have been employed, and are capable of giving satisfactory results when properly handled.

BRITISH NON-FERROUS METALS RESEARCH ASSOCIATION
EUSTON STREET
LONDON N.W.1

(MS. received 13th August 1953)

Reference

- ¹ Silman, H., *Bull. Inst. Metal Finishing* (Spring 1953).

Discussion

Mr. R. L. HILL: Can the lecturer recommend any particular type of abrasive for removing slight surface damage on chromed rollers?

Mr. E. A. OLLARD: It is unfortunately impossible to rectify the damage on a chromium-plated copper roller without removing the chromium. If the surface becomes scratched, the best thing to do is to strip the chromium, carefully polish out the scratch with a suitable abrasive, such as a Tripoli composition, and then re-chromium plate. I do not think that much good can be done on the chromium facing itself.

Mr. H. B. HAMPSON: The lecturer refers to "standard cyanide solution". Would he give us a standard setting for this bath, which he would regard as reliable?

Mr. OLLARD: As mentioned in the paper, any standard copper cyanide bath should be suitable for this purpose. A suitable solution would be as follows—

Sodium cyanide ...	6 oz. per gallon
Copper cyanide ...	4.8 oz. per gallon
Rochelle salt ...	8 oz. per gallon
Sodium carbonate crystals ...	6 oz. per gallon
Temperature ...	130°F.
Current density ...	20-25 amp./sq. ft.

Mr. HAMPSON: Has the lecturer had experience of iron contamination in the copper sulphate bath? If so, can he recommend a satisfactory means of dealing with this problem?

Mr. OLLARD: A small quantity of iron in an acid solution is not usually detrimental. Iron, however, is difficult to remove from this type of solution, since it cannot be deposited out preferentially. If iron contamination is found to be troublesome, it would be better either to make a new solution, or to remove some of the old solution and replace with fresh. In producing printing rollers, however, the solution should not be contaminated with iron, and precautions should be taken to see that this does not happen.

Mr. B. C. VAN NOORDWIJK: Is the high current density mentioned in the preprint possible when putting on thick layers, say $\frac{1}{4}$ in.?

Mr. OLLARD: Very high current densities are possible when depositing copper on printing rollers if the solution is kept warm and the cylinder is rotated at high speed. Current densities up to 1000 amp. or more have been used, but in general these high current densities are not economical, and values of the order of 100-200 amp./sq. ft. will probably be found most satisfactory. Such current densities are found to be satisfactory for producing thick deposits of copper up to $\frac{1}{4}$ in. or more.

Mr. VAN NOORDWIJK: As ordinary electro-deposited copper is rather soft, does the use of

addition agents give a very much harder copper?

Mr. OLLARD: The use of addition agents in an acid copper solution will produce hardnesses very much in excess of that produced from a straight solution. In some cases the hardness figure may be doubled.

Mr. VAN NOORDWIJK: The use of anode bags and of filtering is said to be necessary. Can by very good filtering the use of anode bags be dispensed with?

Mr. OLLARD: It is not essential to use anode bags and quite satisfactory deposits can be produced without their use, provided the degree of agitation at the cathode surface is sufficient to remove any small particle which may lodge on it. Anode bags, however, have the advantage that they stop a certain amount of sludge entering the solution and reduce the choking of filters, etc.

Mr. R. J. HANNAY: What is the effect of the softness or hardness of the deposited copper on the etching qualities of the roller. Depth of engraving is required for textile printing without at the same time increasing the surface area of the design. Does the lecturer imply by his warning about etching difficulties if the hardness of the deposit is greatly increased, that difficulty would be experienced in producing depth of engraving whilst restraining the surface spread of the etching?

Mr. OLLARD: There is at the moment no exact information as to the effect of change of mechanical properties of the copper on the etching qualities. A harder copper has a finer crystal structure and this will etch at a different speed, usually faster. There does not seem to be much information to suggest that it will increase the undercutting on the design, but anything which alters the speed of etching may upset the photo-engraving process unless the people concerned are prepared to make allowances for it. So far as I am aware, there is no method of producing copper which will etch downwards and not sideways.

Mr. J. F. MASTERS: More and more things to-day are being made of "plastics". Does the author know whether printing rollers have been tried? With all the man-made variables available I should think there may be some scope.

Mr. OLLARD: With regard to the possibility of making printing rollers of plastics, this might be possible with a very simple design which could be cut by a machine on to the surface. So far as I am aware, there is no method of etching a photographic design on to a plastic surface and normally where complicated designs are required, it is necessary first to make a metal mould, often by electrodeposition. If this were necessary, there would be little advantage in making the cylinder of plastic unless a large quantity of these cylinders were required.

The Production of Pictorial Effects in Textile Printing

N. W. YELLAND

As occasionally required, photographs, pictures, etc. could be reproduced by printing on textiles in colour or monochrome, if means could be found to engrave intaglio rollers so that they would print precisely the required graduated density of colour at each point of the surface. Experiments are described which were made to ascertain what colour-tones are produced by various strengths of engraving of two possible types—(i) intaglio half-tone (graduated cell-area) and (ii) photogravure (graduated depth of etching). Tone values were obtained by calculation from reflectometer measurements on the prints.

Photogravure grounds could give smoother quality of tone, being potentially less subject to producing thread-moiré effects than is half-tone, but they are less easy to control in practice. Means are described for making intaglio half-tone dot positive films to produce the required tone-rendering with any given combination of cloth and printing colour. The apparatus employs for half-tone conversion a form of half-tone screen in which every aperture is a microscopic lens, in combination with a light-source which is regulated to control the radial distribution of light in the half-tone dots.

A typical experiment is described to ascertain what gamut of mixture-colours can be obtained in three-colour printing on textiles when the colours fall on in the wet state. The Munsell colour-atlas was used for approximate colorimetry in this experiment.

Images in monochrome and in three colours can also be produced on cloth by direct photography from suitable sets of negatives or diapositives.

In printing on paper, pictures and photographs of all kinds, in monochrome and in polychrome, may be adequately reproduced by a variety of processes. Textile printers encounter a demand, slight but persistent, for similar effects to be printed on cloth. The demand arises in various ways, e.g. in the production of souvenirs of places or occasions, such as the coronation festivities of this year, in the reproduction of colour photographs as originals, or in the reproduction of painted originals which contain extensive areas of graded colour-tone.

The value of naturalistic reproductions as textile patterns may be limited, since textiles in use are often made into articles, like garments or curtains, which hang in folds that break up and obscure the detail of the pattern. Pictures of this type are also not easily reproduced by the customary methods of engraving rollers and machine-printing textiles, principally because these techniques, in combination, do not normally include any means of applying the printing colour in regulated densities at different points of the image, so as to produce exactly controlled gradations of colour-tone in the print. In an ordinary calico-printing design, the bulk of the colour is present in the form of large or small areas, each of uniform tone. Other difficulties arise, such as the precise control of register in the multicolour printing of cloth. Also, textiles differ from paper with respect to continuity of surface and absorptive capacity, giving rise to conditions which are opposite to those which prevail in paper-printing, and are inimical to the use of paper-printing methods. If paper-printing machinery were fed with cloth instead of paper, an imprint of sorts would no doubt be produced, but it would in general be unsatisfactory. A possible approach to the problem is to review the methods used for tone-reproduction in paper-printing, and to consider how they might be modified to meet textile-printing requirements, and preferably so as to be usable on ordinary textile-printing machines.

In paper-printing, the applied colour is usually confined to the surface of the material, and therefore normally requires only a very thin film of printing ink, which can be transferred as a thin layer on the surface of the printing forme. In textile printing, on the other hand, a considerable volume of colour has to be applied per unit area to

produce the commercially required degree of penetration into the material; the requisite volume of colour cannot be applied as a mere surface film, but has to be carried in recesses in the surface. It follows that, of the three processes that are commonly used for paper-printing—relief, planographic, and intaglio—only the last is, in general, available for textile printing. The principal technical problem is to produce intaglio-engraved rollers which will print the required tones on cloth.

Hand Stipple

Various tones of colour can be produced with copper printing rollers by the use of stipple-punches to produce engraving grounds in the form of groups of small circular recesses of varying depth, size, and spacing. The process resembles half-tone, though the individual dots of colour may be fused by actually running together on the material as well as by seeming to merge together when seen at a distance. Since the size, depth, and spacing of the dots are all under control, the method is capable of producing a wide range of delicately graded tones when used by highly skilled engravers, but it is relatively slow and expensive, and is not much used for the reproduction of photographic originals.

Photogravure

In a sense, the most appropriate way of printing various tones on textiles is to use a roller in which the areas which have to print the various tones are engraved to corresponding depths. Photogravure (or Rotogravure) is a well known process which uses an engraving of this type for paper printing, and trials have been made to ascertain whether photogravure engraving can be used for textiles. One trial was made to find the depths of engraving required to print various tones, with several printing colours on various cloths. For this purpose a 15 in. \times 12 in. photographic film was prepared, having twelve evenly spaced 2-in. squares photographed on it. Each square contained an engraving ground of 30 lines per inch inclined at 45° to the sides, the opaque black lines on the film, which were to form the engraving grooves, being much wider than the alternate clear lines, which were to form the cell walls or tops. Several repeats of this film were printed on to a roller sensitised to light by being

coated with a "cold-top" enamel, which after light-exposure was developed and converted into an etching resist. In order to produce the required range of engraving depths, each of the twelve squares was etched for a different time, ranging from 30 sec. up to 6 min. by 30-sec. steps. In the film, the width of the clear lines was regulated from square to square according to the time of etching, to compensate for sideways action of the etching mordant and finish with cell walls ("tops") of the same width in all twelve grounds. The engravings were examined, photographed, and measured, in plan and cross-section, under the microscope.

Comparison of the film (Fig. 1A) with the plan of the engraving (Fig. 1B) shows the loss of top width due to side-action of the mordant. The depth of the engraving, seen in the cross-section (Fig. 1C), is of the same order as the side-action. The cross-section shows a wide, shallow, flat-bottomed groove whose shape is very different from that of an ordinary calico-printing ground. For shorter etching times, the depths appear very shallow indeed in the cross-sections. The photographs of the engraving were made after a series of printing trials; the tops are traversed by doctor-scratches, and the grooves are stained with a residue of printing colour.

The results of the microscopic measurements of depth, top width, and colour capacity of the engravings are shown in Table I. The colour capacity of an engraving can conveniently be expressed in terms of the volume of colour contained per unit area of the engraving, and is of the order of 100 c.c. per square metre for an ordinary textile engraving. Alternatively the capacity can be expressed as the thickness of a uniform layer which would have the same volume per unit area, as in the sixth column of Table I; in the case of the present engraving, having wide flat grooves, this measure is only slightly less than the depth of etching (third column).

Various cloths were printed with various colours from the trial roller, and it was found that a range of smooth level tones were produced by the twelve depths of engraving. On certain cloths, however, the "top" of the ground was just perceptible in the

print, and a "moiré" pattern, formed by the incidence of the regular structure of the ground upon the regular structure of the threads, was not entirely eliminated.

REFLECTANCE MEASUREMENTS

The tones produced by the engravings were studied in the first place by means of reflectance measurements on the prints. To enable reflectance to be measured easily and quickly on a large number of samples, the measurements were made with a photoelectric reflectometer, fitted with a barrier-layer photocell screened by a correction filter which had been accurately made to register relative visual luminosities. The typical set of results plotted in Fig. 2 shows the reflectances obtained when a crêpe cloth is printed with yellow, red, green, and black printing colours.

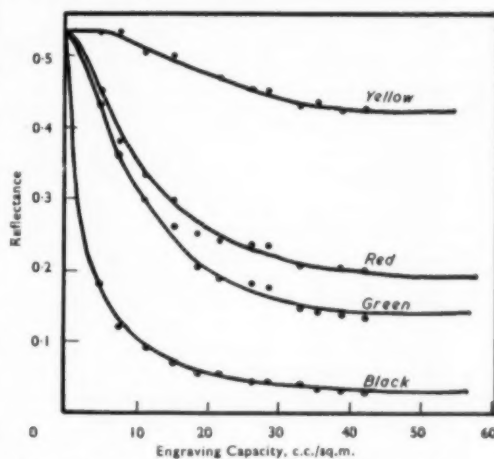


FIG. 2—Trial Photogravure Roller—Relation between Engraving Capacity and Print Reflectance

As the capacity of the engraving increases, the reflectance tends to fall steadily for every colour. The fall is at first rapid, then much slower, but the reflectance is still decreasing at the greatest volumes applied in this trial.

TOPE VALUES

The reflectance values plotted in Fig. 2 do not immediately measure the apparent differences of darkness of the prints. Apparent darkness or *tone value* is not related in a linear way to reflectance, but can be calculated from it. The appropriate definition and the scale of measurement of tone values have been the subject of a number of investigations, e.g. in connection with the tone-rendering abilities of photographic and printing reproduction processes, but it is not known that any final agreement has yet been reached; thus the scale of measurement remains to some extent subject to choice. Two scales have been employed at different times in the course of the present work: one scale is based upon the psychological Weber-Fechner principle, which expresses change of visual response in terms of changes of physical stimulus; and the other is based upon the scale of grey tones of the Munsell colour atlas¹. The two tone scales are very similar; the

TABLE I
"Photogravure" Trial Roller

Square No.	Time of Etching (min.)	Depth of Etching (mil*)	Width of "Top" (mils)	Capacity of Engraving (c.c. per sq.m.)	(mean depth, mils)
0†	0	0	0	0	0
1	½	0.21	2.41	4.9	0.19
2	1	0.32	2.31	7.6	0.30
3	1½	0.47	1.99	11.0	0.43
4	2	0.64	1.66	15.2	0.60
5	2½	0.77	1.63	18.4	0.73
6	3	0.91	1.59	21.7	0.86
7	3½	1.09	1.44	26.2	1.03
8	4	1.20	1.46	28.6	1.12
9	4½	1.41	1.84	33.1	1.30
10	5	1.53	2.14	35.6	1.40
11	5½	1.69	2.34	39.1	1.54
12	6	1.83	2.19	42.2	1.66

* One mil = 0.001 inch

† Unprinted

logarithmic Weber-Fechner scale was used for the measurements plotted in Fig. 2, and will be discussed here.

The requirements to be borne in mind in the construction of a tone scale are—

(i) That the index of tone should be a number which increases with increasing depth of shade (i.e. with decreasing reflectance).

(ii) That equal differences of tone index should correspond with differences of tone which look equal, in different parts of the tone range.

(iii) That the unit difference of tone index should correspond with a readily perceptible difference of tone.

The logarithmic formula adopted for converting reflectances to tone values was—

$$N = 50 \log_{10} \frac{R_0}{R_p}$$

(N = required tone index number; R_0 = reflectance of the unprinted material; R_p = reflectance of the printed material).

The use of this expression is equivalent to assuming that, starting from unprinted material, the tone darkens by one unit step each time the reflectance falls by about 5% (actually 4.7%) of its value. It is also implied that there are about 70–80 steps of tone comprised between unprinted material and the deepest attainable full shade (black) that can be printed on it.

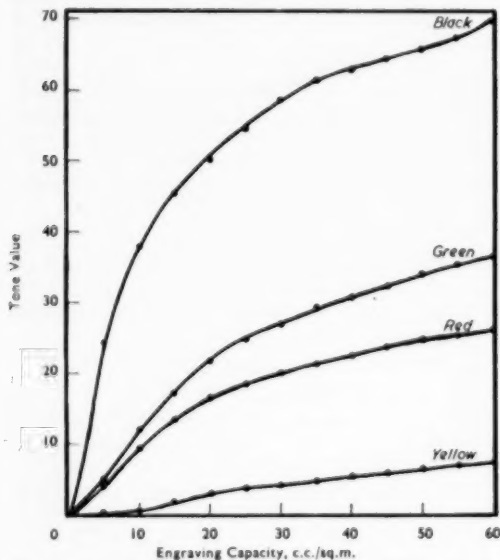


FIG. 3—Trial Photogravure Roller—Relation between Engraving Capacity and Tone of Print

The results shown graphically in Fig. 3 were obtained when the tone values calculated from the reflectances of Fig. 2 were plotted as a function of engraving capacity. The graphs show that, as engraving volume is increased, the tone value increases along a fairly smooth curve, for each colour. The increase of tone is at a lower rate for the larger volumes, but it is still increasing at the highest volume shown in the graph.

CHARACTERISTIC TONE OF AN ENGRAVING

As shown in Fig. 3, the tone produced by a given depth of engraving depends on the colour printed, being, naturally, greater for dark colours than for pale ones. It is, however, of interest in the present connection to ask whether each depth of engraving has a fixed tone-rendering property, independent of the colour printed. For each colour, the tone produced by each engraving was expressed as a fraction of the darkest tone reached with that

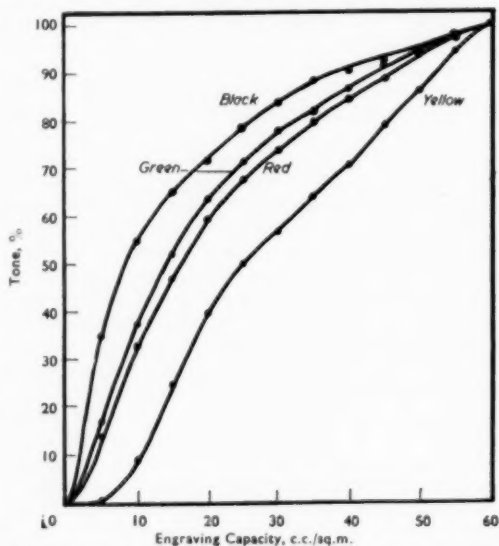
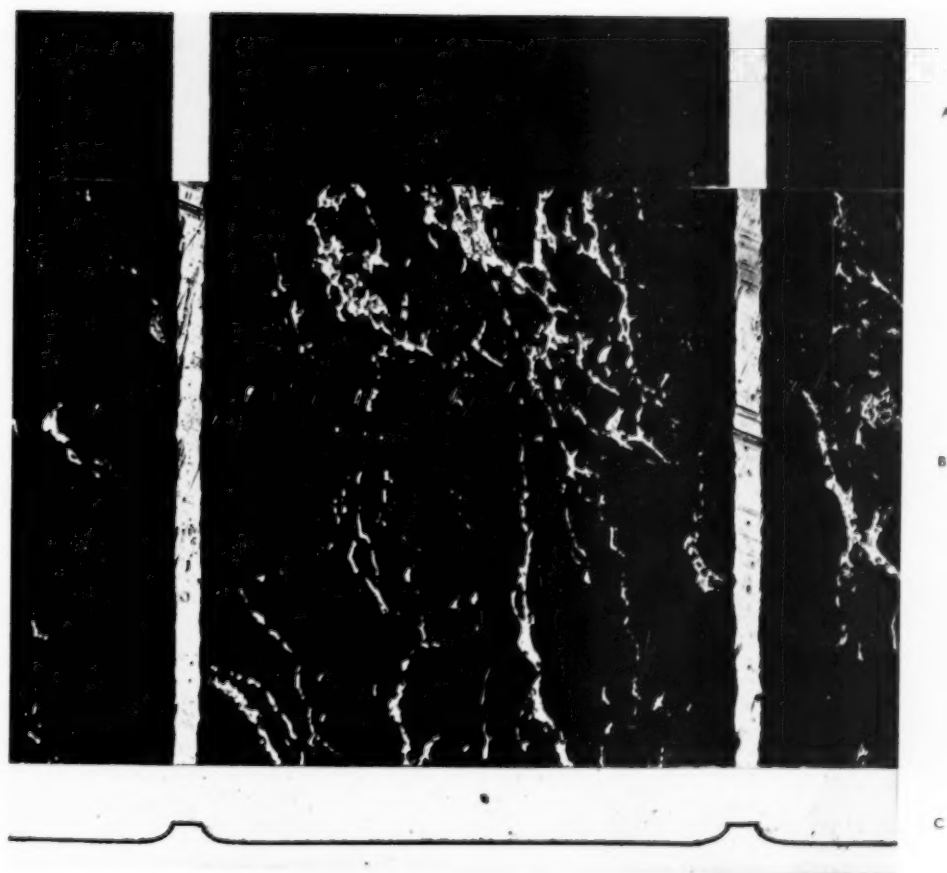


FIG. 4—Trial Photogravure Roller—Relation between Engraving Capacity and Percentage Tone

colour. The resulting curves (Fig. 4) are not coincident, so that percentage tone is not independent of the colour. For example, an engraving of 30 c.c. per square metre capacity gives a 57% tone with the yellow colour and an 84% tone with the black colour.

PHOTOGRAVURE IN PRACTICE

In an actual photogravure roller, the varied depths of engraving are produced by etching through a graded resist formed by exposing dichromated gelatin "carbon tissue" under a positive transparency of the subject. The carbon tissue is usually exposed in flat frames, and is then transferred to the roller for development of the resist and etching. This procedure contributes to the success of the process, since it ensures that the most hardened and exposed surface of the gelatin is immediately in contact with the copper, while the unexposed layers are accessible for selective removal by the warm water in developing. The conditions are not, however, very convenient for textile engraving, where there may be several repeats of the pattern on the roller surface, where it is essential to avoid any appearance of "joins" in the pattern, and where exact register must be maintained in the case of multicolour patterns. Also, as shown by the preceding results, it may be necessary to etch to depths greater than 2 mils to obtain a full shade, and such depths are difficult to attain when etching through a photogravure resist.



- A—Part of line ground diapositive film
- B—Plan view of engraved ground
- C—Cross-section of cast of engraving

FIG. 1.—Composite Photomicrograph of Trial Photogravure Engraving Ground etched for 4 min. ($\times 1000$)

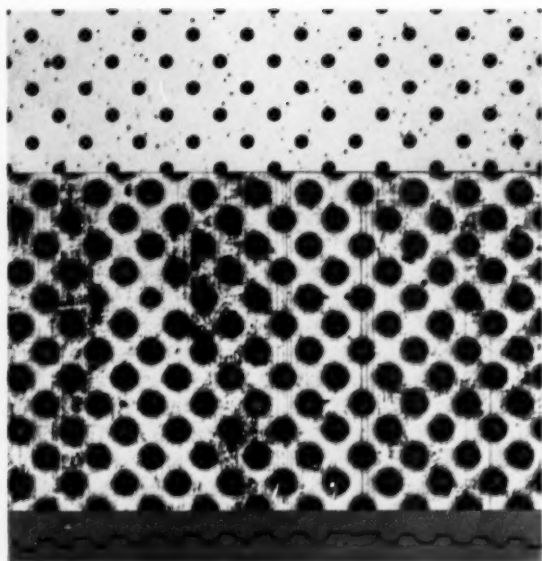


FIG. 5—5-mil Dots

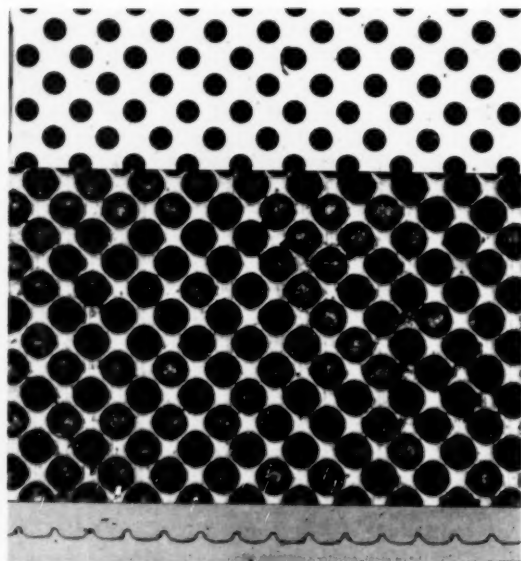


FIG. 6—9-mil Dots

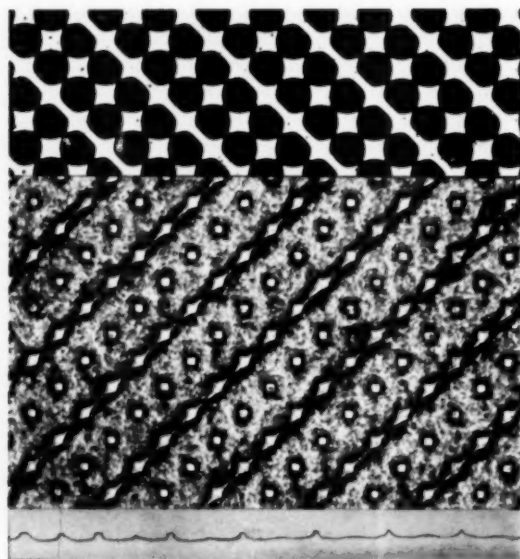


FIG. 7—14-mil Dots

FIG. 5-7—Intaglio Half-tone Film (65 scale), Etched Ground, and Cross-section

For textile engraving, it would be more convenient if the roller itself could be coated with the light-sensitive colloid before light-exposure; this, however, would introduce new problems, because it would reverse the favourable relationship of the exposed and unexposed layers of the resist. Nevertheless, processes on these lines have been devised², and trials of three- and four-colour reproduction of colour photograph originals by this method have given results which display a certain degree of promise. (Examples displayed.)

Intaglio Half-tone

It has been noted that photogravure has certain drawbacks for textile engraving; the process of photogravure etching, with a series of mordants of diminishing concentration, might also prove difficult to control in the way required for textiles as opposed to paper-printing, for which the practice is established. An alternative method of producing intaglio tone-printing rollers—called *intaglio half-tone*—has also been explored. Instead of making all the engraving cells about the same in area, and varying their depth to produce the various tones, no attempt is made to control directly the depth of etching, but the area of the engraving cells is controlled. The advantage is that etching is greatly simplified, since the same etching treatment can be given to the whole surface of the roller. In a typical trial, a half-tone companion to the "photogravure" trial roller was engraved as follows—

A photographic film was prepared, bearing an image composed of twelve separate two-inch squares, each occupied by an engraving ground consisting of evenly spaced circular opaque dots on a transparent background. The dots were from a cross-line screen of 65 lines per inch, their nominal diameters being given in Table II.

TABLE II

Square No.	1	2	3	4	5	6	7	8	9	10	11	12
Dot diameter, mils	3	4	5	6	7	8	9	10	12	14	16	18

A dot 3 mils in diameter was the smallest that could be consistently engraved by the method employed; the diameter was increased by 1 mil per square up to 10 mils, and then by 2 mils per square up to 18 mils, in the region where the change of tone is slower. Dots up to 12 mils in diameter do not touch one another (at 65-scale spacing), but dots larger than 14 mils are joined. When a ground formed of such joined dots is etched, the "top", i.e. the parts of the non-printing surface left between the dots, is reduced to isolated pins, and does not afford adequate support for the cleaning doctor. In order to provide this support, a continuous-line ground was added to the film diapositives. The lines of this ground pass at 45° between alternate diagonal rows of dots, and show only in the squares in which the half-tone dots are otherwise large enough to join.

The diapositive film was printed down in several repeats on to a roller in a cold-top enamel, and the image was etched into the roller for 6 min. in ferric chloride solution of 45°Tw., at 78°F., with rotation at 200 r.p.m. The series of engravings thus produced in the roller were compared by forming

celluloid-cast replicas of the engraved surface for examination under the microscope in plan and cross-section. Fig. 5-7 illustrate the microscopic character of the engravings, for panels of dots of diameter 5, 9, and 14 mils respectively. In each case the upper section of the figure is a photomicrograph of part of the film diapositive; the middle section is a corresponding photomicrograph of the cast of the engraving, showing by comparison the enlargement of the dot produced in etching; and the lower strip is a photomicrograph of a cross-section of the celluloid cast, showing the depth and shape of cross-section of the etched recesses.

The depth and the colour-capacity of the twelve engraving grounds were determined in a series of measurements under the microscope. In these results (Fig. 8) the depth of etching is simply the

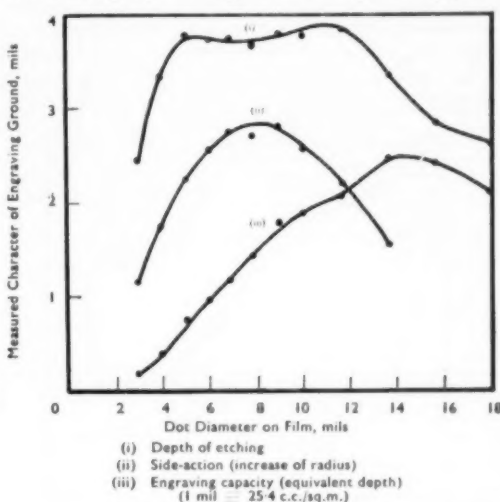


FIG. 8.—Intaglio Half-tone Roller—Measured Characters of Engraving as Functions of Dot Diameter on Film

maximum depth of the recesses, measured to the bottom of the etched cells. The side-action is the increase of radius of the etched cells as compared with the radius of the diapositive dots. The colour capacity of the engraving is expressed in terms of the thickness of a uniform layer which would have the same capacity as the engraving.

The results are of interest in relation to the technique of etching. It is seen in the first place that, although all squares of the roller have had the same etching treatment, the depth is not the same everywhere, but varies in a way that tends to reinforce the tone variation imposed by the dot areas. The depth is small for the smallest dots, but is greater and roughly constant for dot diameters from 5 to 12 mils. For larger dots (which are joined dots showing the additional line ground for doctor support) the depth decreases again very markedly. The side-action (spread of the dots in etching) is also small for small dots, increases smoothly to a maximum for 8-mil dots, and thereafter decreases smoothly again for larger dots. The capacity variations represent the combined effects of variation in dot diameter, depth, and side-action. The volume is of course small for small dots, and

increases almost linearly when the dot diameter increases from 3 to 9 mils. At this point the slope decreases abruptly, but the rise continues to 14 mils, when the volume commences to fall, probably owing to the decrease in etching depth. These changes of etching depth and side-action, which accompany changes in the dimensions and shape of the diapositive film dots, are probably associated mainly with consequent variations of the stirring action which the etched ground exerts on the etching mordant, and partly also with local variations of chemical exhaustion and activity of the mordant.

The engraved roller was used to print various cloths with various printing colours. The tones produced were studied by reflectance measurements and calculation of tone values. The reflectance measurements are plotted as a function of engraving capacity in Fig. 9. For every colour, reflectance is still falling at the highest densities of colour applied. Tone values calculated at regular intervals of engraving volume by interpolation from Fig. 9 are

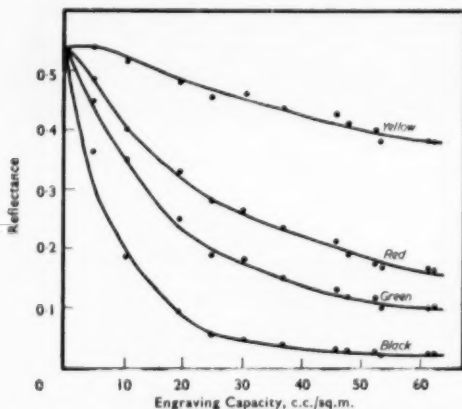


Fig. 9— Trial Intaglio Half-tone Roller— Relation between Engraving Capacity and Print Reflectance

shown in Fig. 10, and the percentage tones are plotted in Fig. 11. As in photogravure, the percentage tone of a given engraving is not independent of the colour which it is to print. The average graph is shown in Fig. 11. The tone increases slowly at first, but is not zero for 3-mil dots; it increases more rapidly up to about 6 mils, and then more slowly up to about 13 mils, after which there is no further increase of tone up to 18 mils. The flattening of the curve in this region is due principally to the fact that the engraving volume does not increase indefinitely with increase of dot diameter (Fig. 8). The greater part of the attainable tone range is produced by dots between 3 and 13 mils in diameter. The shape of the curve is not otherwise very favourable for control of tone rendering. What can be directly controlled in a half-tone process is the diameter of the dots; it would be convenient if, for example, tone were directly proportional to diameter. It obviously is not proportional: the tone rushes up most steeply for the smallest dots, which are the most difficult to control, and increases relatively slowly for the larger dots.

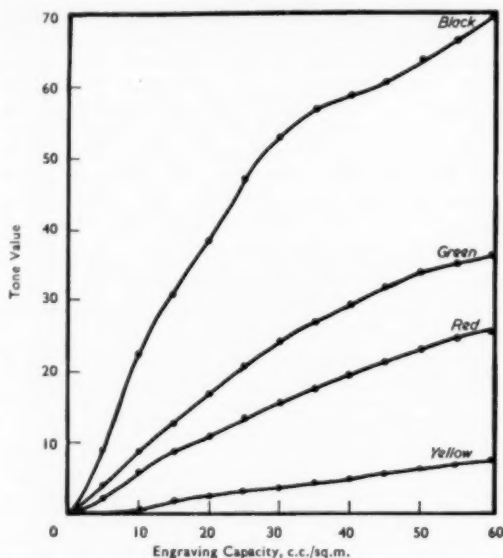


Fig. 10— Trial Intaglio Half-tone Roller— Relation between Engraving Capacity and Tone of Print

A good deal of work is engraved by intaglio half-tone methods; the tone-rendering in general leaves something to be desired. Difficulties are also encountered owing to the formation of moiré patterns by the superposition of the regular structure of the half-tone screen upon the nearly regular structure of the threads in the cloth.

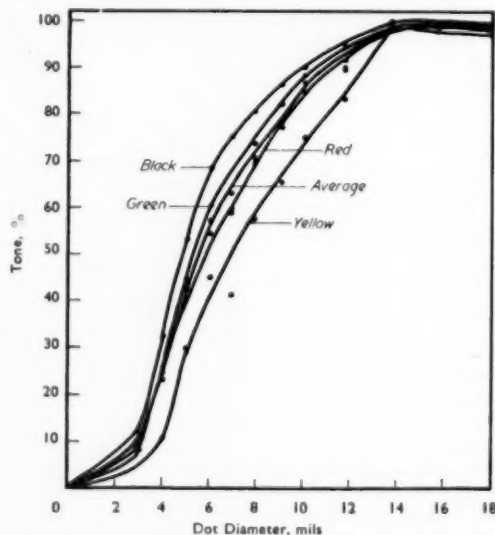


Fig. 11— Trial Intaglio Half-tone Roller— Relation between Dot Diameter and Percentage Tone

HALF-TONE CONVERSION

Continuous-tone originals, like photographs for example, are most often translated into half-tone form (evenly spaced microscopic dots of various sizes) by means of a well known device called the *half-tone screen*, used in a process camera. The screen, and the theory and practice of its application,

are described in textbooks of process-engraving³. It is explained that the effect of the screen is to break up the image in the camera into dots of light which are not sharp-edged, but have a certain radial gradation of light-intensity. The ability of the process to convert various intensities of light into corresponding sizes of silver dot in the photograph depends essentially upon the presence of this radial gradation; further, the tone-rendering properties of the process in detail depend upon the details of the radial gradation. The optics of the system by which the gradation is determined have been the subject of several investigations, including recent ones⁴, but are still to some extent in dispute. The consensus of opinion appears to be that, for screens of coarse scale, the radial distribution of light within the half-tone dots can be calculated with sufficient accuracy from penumbra theory, assuming the rectilinear propagation of light, while for screens of fine scale (many lines per inch) the openings are so narrow that perceptible diffraction effects are produced, so that the wave character of light has to be taken into account in the calculation.

In practice, when making a half-tone translation to suit the tone-rendering peculiarities of any process (relief or lithographic printing) under given conditions, the effective radial gradation of light-intensity in the dots is regulated by means of a variety of expedients and devices used in conjunction with the camera. In trials on the use of intaglio half-tone, these devices were also employed, but it was found that satisfactory tone rendering was in general difficult to obtain consistently. For example, reference to results like those of Fig. 11 showed, in one case, that the dot diameters in Table III were required to produce a series of tones. It was

TABLE III

Percentage of full tone	20	40	60	80	100
Required dot diameter, mils	3.7	4.9	6.5	9.1	14

found that, when the dot positive was made from a continuous-tone negative of the original, the negative of these tones did not in general produce these corresponding dot sizes, and this situation could not be corrected by means of the devices commonly employed. It is to be noted that the controls in question are not relied on entirely, even in relief or lithographic half-tone, but further corrections are applied, e.g. by fine etching or staging in the etching of relief half-tone blocks, or by analogous processes of "dot etching" in lithography. In textile printing, there may be several repeats of the pattern on each roller; also no intaglio fine etchers were available. Accordingly, it was desired to work if possible by means of completely straightforward etching, without local correction at that stage.

Alternative forms of half-tone screen, called *contact screens*, have lately become available; these produce the radial gradation in the dots by means of a graded density in the open meshes of the screen. Since this density is in the form of a magenta dye, its effective contrast can be varied by varying the colour of the printing light. This is of some assistance, but did not appear to be a complete solution, since the type of radial variation still remains fixed.

The position was, therefore, that the series of dot diameters required to represent the various tones in any given case of intaglio printing could always be specified, and that these dimensions varied from one case to another. On the other hand, the available means of control did not enable the required dot sizes to be produced, because they did not establish the required control over the radial distribution of light in the dots. In any given case, the required distribution could readily be calculated on certain assumptions, and it was decided to examine possible methods of controlling the radial distribution in practice in a direct, precise, and convenient way.

Method of Half-tone Conversion

The essence of the method adopted⁵ is to use, instead of an ordinary half-tone screen, a special form of screen in which every aperture is a microscopic lens, capable of forming a distinct real image (or in some cases a line focus) of an external object. The screen is set up facing a distant source of light, in which, by some convenient means, the required radial distribution of light is reproduced on a much enlarged scale. Each aperture of the screen then focusses on the photographic plate a microscopic image of the light source; in every image the required radial distribution of light is reproduced on the requisite microscopic scale.

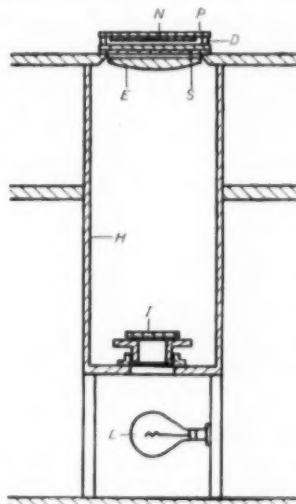


FIG. 12—Projection Shaft for Half-tone Conversion

The arrangement of the apparatus is shown in Fig. 12. The half-tone screen *S* is supported horizontally over a hole in a table in a dark room. The photographic plate *P*, on which the half-tone dot image is to be formed, rests on a set of distance-pieces *D*, which support it at the correct height above the screen so that the dots are sharply focussed on the plate. The continuous-tone negative *N*, which is to be converted into a dot positive, is strapped to the underside of the plate *P*. A light-tight shaft *H* extends vertically downwards from the table top, and encloses the light-source *I* at its far end, on a lower floor. The light-source is a disc

of opal glass about 6 in. in diameter supported in a ring which can be revolved at a steady speed by a motor. The disc is illuminated from below by a lamp L , and the radial distribution of light in it is controlled by a mask, which is fixed to the revolving disc, and which is so shaped as to have a prescribed angle of opening at each radius of revolution. A large collimator lens E may be placed at the top of the shaft if required to prevent any slight enlargement of the projected image by the divergent light-beam.

Adjustment of Radial Sectors in Practice

The requirement for correct tone rendering in any particular case is that each transparency in the continuous-tone negative should produce a specified dot size, and this requires that the light-intensity in the half-tone dot should have a specified value at each radius. The required radial distribution is reproduced on a large scale in the six-inch disc by means of a revolving clear aperture in an opaque surround, which has a specified angle of opening at each radius. The form of distribution can be conveniently varied by adjusting the shape of the sector opening, and the various types of distribution that are required to suit different combinations of cloth and printing colour can readily be obtained by means of a stock of interchangeable sector masks.

For each cloth and printing colour that are of interest, the form of radial distribution of light, needed to produce the required tone rendering, is determined by means of a trial print with the standard roller, combined with measurements of the transparencies in a negative of a tone scale. The required radial distribution is then calculated on the simplest assumption, namely that the edge of every dot is a contour of fixed light-intensity. The sector so calculated and cut is tested, to ascertain whether it does in fact produce the requisite relationship between light-intensity and dot size, by means of an exposure trial in which duration of exposure is varied instead of light-intensity. In some instances, the sector is found to produce a sufficiently close approximation to the required effect; but in other instances, particularly if the required curve relating dot size and light-intensity has any sharp inflection, there may be some divergence between the required curve and that actually yielded by the sector as first calculated. The error can be corrected empirically, by comparing the two curves and calculating the required corrections, either by adjusting the sector opening at each given radius (intensity correction) or by adjusting the radius at which each intensity is given (radius correction). The two corrections produce similar effects, but are not exactly equivalent. A sufficient total correction is usually obtained by applying in succession one correction of each kind.

Calculation of Radial Distribution

The process for making an intaglio half-tone roller from a continuous-tone original consists in the following steps—

Stage 1—A continuous-tone negative is made of the original, usually by photography in a camera.

Stage 2—A half-tone dot positive is made from

the continuous-tone negative. This is called the stage of "half-tone conversion".

Stage 3—The half-tone dot positive is printed down to the roller surface, and etched into it, giving the required printing surface.

In stage 1, under fixed conditions of photographic processing, each tone in the original gives rise to some corresponding density (therefore light-transmittance) in the continuous-tone negative. (The relationship between original tone and negative transmittance is determined experimentally.)

In stage 3, under fixed conditions of engraving, etching, and printing, each dot diameter in the half-tone dot positive gives rise to some corresponding tone respectively in the eventual print. (The relationship between dot diameter and print tone, for each cloth and printing colour, is also determined experimentally, as in the examples given and displayed.)

Thus, in order to establish some required fixed relationship (for example, equality) between the tones of the original and the tones of the final print, it is necessary and sufficient to ensure that, in stage 2, each transparency existing in the continuous-tone negative, gives rise respectively to some prescribed dot diameter in the half-tone dot positive.

The dot diameter which is in fact produced by each transparency of the negative respectively, is determined by the radial distribution of intensity in the light-dots which the half-tone apparatus projects upon the photographic plate in stage 2.

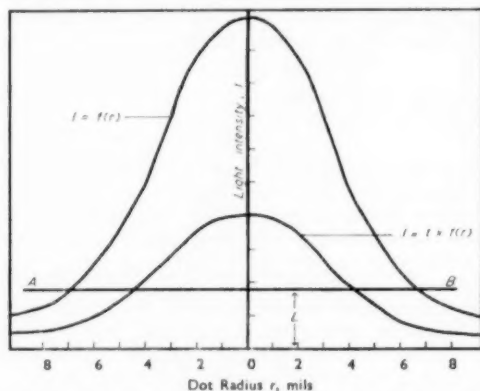


FIG. 13—Radial Distribution of Light Intensity in a Half-tone Dot

Fig. 13 represents a "cross-section" of a light-dot in which light-intensity I is plotted vertically at each radius r plotted horizontally. The upper curve represents the distribution of light in all the light-dots when there is no continuous-tone negative in the apparatus. The lower curve represents the distribution with a negative in place, at a point of the negative where the transmittance is a fraction t .

If the intensity in the upper curve is represented as a function of radius—

$$I = f(r) \quad (i)$$

then the intensity in the lower curve is given by—

$$I = t \times f(r) \quad (ii)$$

In the sequence of photographic processes involved in making the dot positive plate, the latter is first developed and fixed, producing fringed dots, whose density naturally varies from a maximum at the dot centre to zero at the edge. The plate is then "reduced" chemically (usually in Farmer's ferricyanide-hypo reducer); by this means the dots are "cut" and rendered more sharp-edged, by removing all the fringes of the dots up to a certain level of photographic density. The effect of this treatment on the dot diameters can be represented in the diagram by drawing the line *AB* at a corresponding fixed level of light-intensity *L*. The dots thus "cut" are converted into sharp-edged discs, sensibly opaque from centre to edge, by intensification or by copying on to contrasty photographic material.

The diameter of dot, produced by each light-transmittance of the continuous-tone negative, is given by the intersection of the line *AB* with the corresponding curve $I = t \times f(r)$. The practical requirement is to determine the value of $f(r)$ at each radius *r*, given the other factors.

At any radius in any dot, we have $I = t \times f(r)$, but if the radius *r* is the edge of an eventual sharp-edged dot, we know that $I = L$ (a constant), hence at the dot edge—

$$t \times f(r) = L \quad (\text{iii})$$

whence—

$$f(r) = \frac{L}{t} \quad (\text{iv})$$

L is a constant, and can be given any convenient fixed value. The negative transmittance *t* for each dot radius *r* is known as follows—

For each radius *r* of final dot-size, the tone produced in the print is known experimentally (from the printing trials on stage 3). The required corresponding tone in the original (it may be the same tone for example) is thus determined, hence the transmittance *t* of the negative is also known experimentally from the trials on stage 1. Thus, for each dot radius *r*, *L* and *t* are both known, and the relative intensity $f(r)$ can be calculated from the simple expression (iv).

Each radius *r* in the half-tone dot corresponds with some radius *R* of the revolving sector in the half-tone apparatus ($R = M \times r$, where *M* is the minification of the images projected by the half-tone screen). Thus, finally, the relative angle of opening of the revolving sector at each radius *R* is equal to a constant *L* divided by the negative transmittance that is required to produce a dot of radius *R/M*. The angle of opening is usually made 270° at the centre, to give a mechanically strong shape of mask.

Fig. 14 shows the comparison between the required curve of exposure plotted against dot diameter and the curve actually obtained from a sector which had been corrected in two stages in this manner. The agreement is fairly close; the principal outstanding divergence is that the actual curve does not rise quite so steeply as required at the highest intensities.

This difference, like some other effects that are encountered, is probably associated with redistribution of light in the dot image by diffusion of

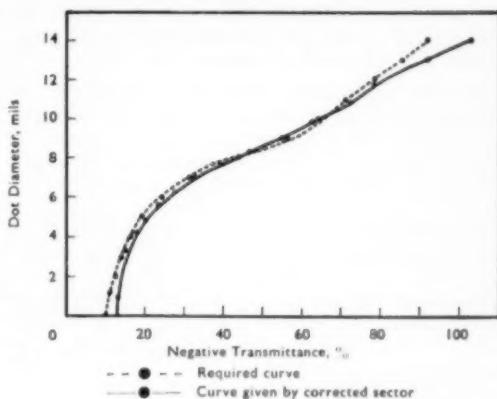


FIG. 14—Half-tone Conversion—Relation between Light Intensity and Dot Diameter

light in the gelatin layer of the plate. It is also possible that the light-intensity at the edge of the dot may not be, as assumed, the same for small dots as for large ones. Within certain limits, the effects of these factors can be compensated for by the empirical method described.

The overall accuracy of the reproduction is tested in the usual way by reproducing a scale of neutral greys. It is found in the majority of cases that the tone rendering is reasonably good; nevertheless the general quality of the printed tones is sometimes unpleasing. The most prominent fault in the prints is described as *moiré*: i.e. the appearance of alternating light and dark bands, in areas which should be of even tone, due to the superposition of the regular pattern of the screen dots upon the regular pattern formed by the weave of the cloth. The *moiré* pattern can be avoided or modified in various ways. It is often possible to suppress it by choosing a suitable number of lines per inch in the half-tone screen, and a suitable angle between the directions of the screen lines and the warp and weft of the cloth; the appearance is, however, often very sensitive to slight changes of this angular adjustment, and accordingly can be upset by skew running of the cloth or by skewed weft. Certain arrays of dots, e.g. the engraver's seven-pin grouping, are sometimes less liable to produce *moiré* on certain cloths than the cross-line array, and can be used instead of it. Cross-line rulings with the lines at 60° instead of 90° also have an advantage in some cases. But even when all precautions have been taken, and actual *moiré* thus avoided, the prints have a somewhat specky, mealy appearance, the effect produced by a dot of given size being different according as it happens to fall on the crest or in the hollow of the thread intersections.

It may be noted that this last observation suggests that it is possible to visualise a system of half-tone for textiles, in which no half-tone screen is used, but the intersecting threads of the cloth themselves produce the half-tone structure. An obsolete style of printing, known as *tipping*, was arranged to apply colour at the crests of the interlacing threads. The effect occasionally varied from point to point in an objectionable way according to

the pressure conditions; tone effects could be produced if such pressure conditions could be regulated in a controlled manner.

It is also to be noted that the faults of mealy tone and moiré, in intaglio half-tone, arise chiefly because one is attempting to produce varied tones by printing colour of a fixed concentration in varied volumes. A much better system for textile printing would be one in which the colour is printed at constant volume for all shades, but in varied dilution. A few trials have been made in which a half-tone paste roller, which carries a negative of the colour-image, is printed on top of the half-tone colour roller. As might be expected, the results were not of much interest, and the subject has not been further explored.

Colour Gamut in Multicolour Work

An original which is an ordinary monochrome photograph can be reproduced by printing from a single roller, but if the original is a painting or a colour photograph, multicolour printing is required, and the question arises as to how many rollers are needed. In printing on paper, it has been found that reproduction of the many and varied colours and tones of most originals can be secured by printing only three colours so that they mix in various quantities and proportions; this is the basis of three-colour processes, though a fourth printer—black—is often added.

When three-colour printing is employed for textiles, by either half-tone or photogravure processes, a question of particular interest is what gamut of mixture colours can be produced by printing with the best available three-colour primaries. The conditions differ from paper-printing in an important respect. In three-colour half-tone on paper, for example, each colour is dried on the paper surface before the next is applied, and the colour-dots can be regarded as small discs of superimposed colour filters. On the other hand, textile-printing machines do not as a rule provide any facility for drying the cloth between successive rollers, and the colours fall on and mix in the wet state. Nevertheless, a range of mixture colours would still be produced, and it is of interest to examine what those colours would be.

In a typical trial, intaglio half-tone engraving was used. Three rollers were engraved, one with repeats of a six-inch square in five weights of engraving, one with groups of horizontal stripes 6 in. \times $\frac{7}{8}$ in. arranged to fall on the six-inch squares, and one with corresponding groups of vertical 6 in. \times $\frac{7}{8}$ in. stripes, placed so as to fall across the horizontal stripes of the other roller. The range of dot diameters in the intaglio half-tone ground was the same on each roller, namely 0, 3.7, 4.9, 6.5, 9.1, and 14 mils of 65-scale cross-line dots, these steps of diameter having been found in a previous experiment to give equal steps of tone (Table III). Printing trials were made, using these rollers, on various cloths, and with various combinations of three printing colours. The latter were chosen with reference to the colours of three-colour inks used for paper-printing, and for maximum brilliance

(saturation). For example, in one trial the dyes were—

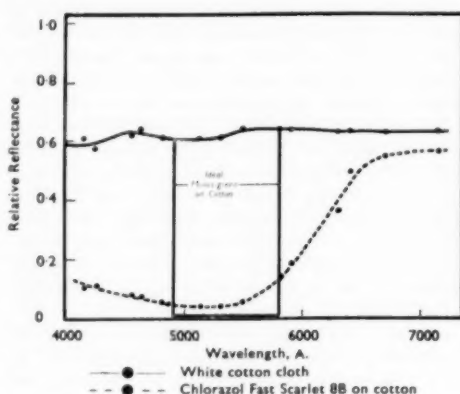


FIG. 15—Spectral Reflectance Curve of Magenta Primary

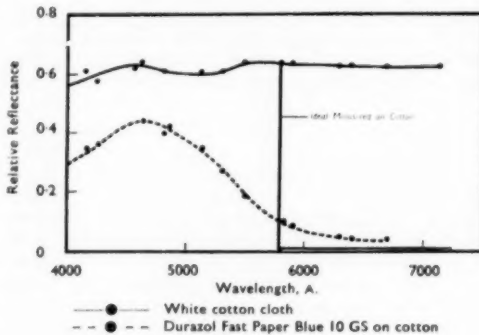


FIG. 16—Spectral Reflectance Curve of Cyan Primary

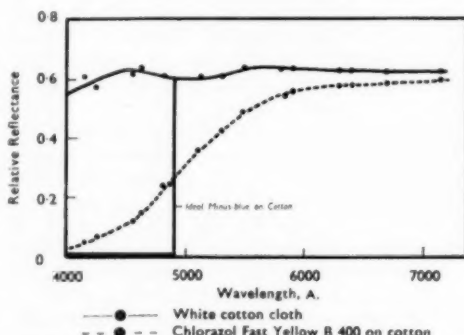


FIG. 17—Spectral Reflectance Curve of Yellow Primary

Magenta primary (minus green)	... Chlorazol Fast Scarlet 8B (ICI)
Cyan primary (minus red)	... Durazol Fast Paper Blue 10 GS (ICI)
Yellow primary (minus blue)	... Chlorazol Fast Yellow B 400 (ICI)

In the printing trial, each of six weights of each dye was combined with each of six weights of the other two, giving in all 215 combinations of colour. The colours of the primaries were recorded in a

spectrophotometric examination, which gave the results shown in Fig. 15-17. The colours of the resulting mixtures were recorded by comparison with the samples in a Munsell colour atlas. A good range of mixture colours was produced; those which were obtained by combinations of roughly equal weights of all three colours were naturally greyish or dull. Particular interest attaches to the more brilliant group of mixture colours that are obtained by combining the primaries in pairs. These yield a range of colours extending in hue fully around the colour circle, with varying saturation; the point of interest is the saturation obtainable at each hue, compared with the saturation of the primaries.

Fig. 18 is a polar diagram in which saturation, measured in Munsell chroma steps, is represented by the radius, hue being represented by position around the colour circle in Munsell hue steps. The figure obtained by joining the points for the colours of maximum obtainable saturation at each hue encloses the gamut of colours obtainable with the chosen primaries, at the adopted level of brightness (Munsell value). The Munsell scales of measurement are useful in this connection because they are adjusted to be scales of equally perceptible steps of hue, saturation, and lightness.

It is seen in the diagram that the maximum obtainable saturation varies considerably around the colour circle, being in general lower for mixture colours than for the unmixed printing colours themselves. This defect is due to the limited saturation of the printing dyes, which in turn is

due to the shape of their absorption curves. As shown in Fig. 15-17, the reflectance curves depart more or less widely from those which would be possessed by ideal colours of maximum colouring efficiency. These, which are not realised by any known dye, are box-shaped with vertical sides⁶. The brilliance of these ideal colours greatly exceeds that of the actual primaries and mixture colours, and cannot conveniently be plotted in the polar diagram (Fig. 18), in which they would lie about twice as far out from the centre as any of the colours shown. From the point of view of colour printing, the defect is, however, not as serious as this comparison would suggest, since the colours of maximum brilliance do not normally occur in the originals given for reproduction.

The ability to reproduce a wide gamut of colours around the whole of the colour circle could be considerably increased if the number of printing colours were greater than three. The reasons why three or four impressions are made to suffice in paper printing is largely a question of cost. Textile printers are, however, accustomed to work with more than three printing colours, and could use the greater number if the correctly engraved rollers could be provided. A difficulty arises here: if three primaries are used, there is only one combination of them that can give the nearest attainable approximation to any given colour of the original; hence a purely automatic system of photography and masking correction can in principle be employed to control the engraving of the three rollers. If, on the

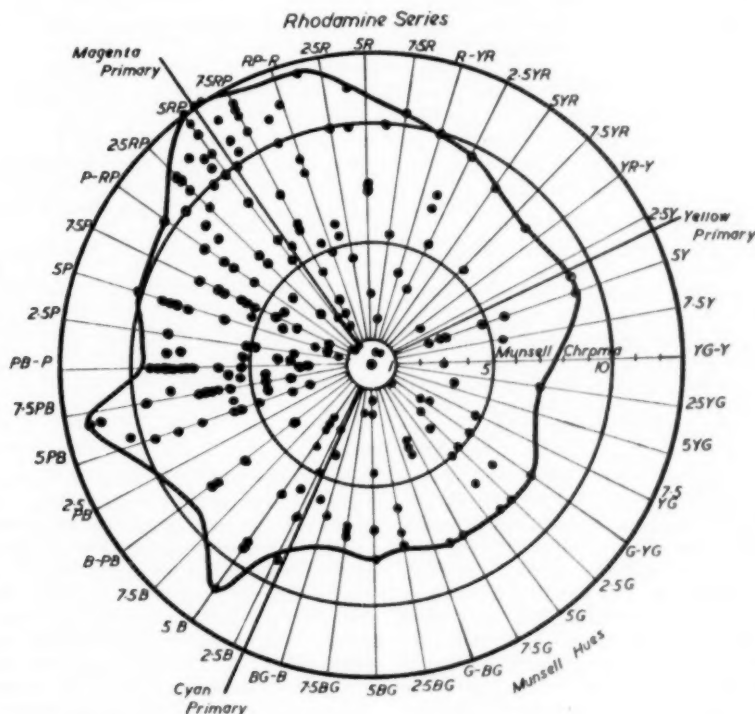


Fig. 18—Three-colour Prints on Cotton—Polar Diagram of Munsell Measurements, showing Gamut of Mixture Colours

other hand, more than three primaries are used, there may be more than one combination of the printing colours that can match any given colour, so that an element of arbitrary choice is introduced. But this difficulty does not appear to be insurmountable, and it is probable that improved systems of colour separation based upon a zoning division of the colour circle could be developed, for use when the number of primaries is greater than three. Systems for this purpose have already been devised for the control of the black printer in four-colour work. Improvement could also be sought by way of a different choice of colours for the printing primaries; in particular, it appears that the use of pigment pastes to confine the applied dye more closely to the surface of the cloth might have important advantages.

Photographic Printing on Textiles

Photographs, etc. can be reproduced on cloth without the use of a conventional type of printing machine at all, by impregnating or coating the cloth with a light-sensitive substance, and exposing to light under a negative or diapositive of the image to be reproduced⁷. Images in monochrome can be produced without essential difficulty; even continuous printing in joined repeats is possible by means of transparent rollers with the light inside. Three-colour printing, required for the reproduction of coloured pictures, offers considerable difficulty in accurately registering the successive impressions, because of the likely stretch or shrinkage of the cloth in chemical processing in the wet state. The patent⁷ proposes to overcome this difficulty by holding the cloth rigidly during the three light-exposures, and not washing the material until the final exposure has been made. Trials by these methods show considerable promise. Apart from the construction of machinery for routine production, a point requiring attention is the preparation of suitably balanced and corrected sets of three-colour negatives.

Future Prospects

The following considerations may affect the development of these possibilities in the future: Intaglio half-tone is the easiest method of pictorial production, and is the method most widely practised at present. It is easily capable of considerable improvement in regard to control of tone rendering, but it is likely that the dry mealy quality

of the middle tones, and the risk of formation of moiré pattern, will stimulate the search for alternative methods that are free from these objections. It appears that photogravure methods may be capable of adaptation in the required way, and there is also a possibility of hybrid processes that combine some of the features of half-tone and photogravure. But all such processes, which operate to produce tone effects by restricting the volume of printing colour applied per unit area, also tend to produce a dry grainy quality of mark, and are likely to enjoy only a restricted acceptance for this reason. No process, applicable to textiles, is known which operates on the opposite principle, by applying a fixed volume of colour at varied dilutions. Processes which produce colour by light-exposure are free from some of these drawbacks, and seem likely to receive increased attention in the future.

* * *

The illustrations for this paper were prepared by Miss G. M. Frowde and Miss J. Burrige, of the Research Department of the Calico Printers Association Ltd. I am indebted to Mr. G. S. Hibbert, Head of the Research Department, for his help and encouragement in the work described, and to the Directors of the Association for permission to publish the results.

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(MS. received 16th May 1953)

¹ Newhall, Nickerson, and Judd, *J. Optical Soc. Amer.*, **33**, 406 (1943).

² Bekk and Kaulen, *BP* 458,968.

³ See e.g. Clerc, L. P., *Ilford Manual of Process Work* (London: Ilford Ltd., 3rd edition 1941), p. 161.

⁴ Harrison, V. G. W., *Photographic J.*, **92 B**, 74 (May-June 1952).

⁵ Calico Printers Assocn. Ltd. and Yelland, N. W., *BP* 653,564.

⁶ MacAdam, D. L., *J. Optical Soc. Amer.*, **25**, 249, 361 (1935).

Collins, R. B., and Giles, C. H., *J.S.D.C.*, **68**, 421 (Nov. 1952).

⁷ Calico Printers Assocn. Ltd., Isherwood, F., and Miller, W. S., *BP* 653,698.

Discussion

Mr. B. C. VAN NOORDWIJK: What fineness of screen can be allowed, taking into account the much greater depth of engraving required for cloth as compared with engraving for paper printing?

Mr. YELLAND: In ordinary textile printing, engraving of considerable depth and therefore of coarse scale (say 35 lines per inch) has to be used for thick cloths, in order to carry a sufficient volume of colour to produce the required thoroughness of saturation of the cloth, while engraving of finer scale (say 55 lines per inch) can be used for lighter cloths.

In the case of graded tone engravings of the

gravure type, the scale of the ground does not have to be fixed on quite the same basis. The depth of engraving is regulated according to the tone required at each point, and is generally much shallower than an ordinary "solid", as described in the present paper. A ground of coarse scale (30 lines per inch) can be either very shallow, to print a pale tone, or deep enough to print a full tone. The scale of the cross-line gravure screen can conveniently be fixed by reference to the fineness of detail in the original given for reproduction. Since fine details cannot in any case be reproduced on coarse cloth, the screen scale

becomes related once more to the coarseness (threads per inch) of the cloth. A screen of 30 to 50 lines per inch can generally be used. The selection of scale and angle of the screen have to be adjusted to minimise moiré formation.

MR. VAN NOORDWIJK: Is the special apparatus used for changing continuous tones in half tone mentioned in the preprint already in practical use?

MR. YELLAND: The apparatus for half-tone conversion described in the paper has been used hitherto for experimental work, and is not yet in everyday routine use.

MR. VAN NOORDWIJK: Usually small points etch deeper in the same time than large points. What can be done to overcome this effect?

MR. YELLAND: The relationship between dot diameter and depth of etching, under the conditions of the experiment described, is shown in Fig. 8 of the present paper. (Curve 1). It is shown that the smallest dots and the largest dots both etch less deep than dots of medium diameter, which etch all to nearly the same depth. The differences in etching depth, which are due essentially to factors governing the circulation and turbulence of the mordant, are not easy to control by any simple modification of the etching technique. But, since the differences of depth are important chiefly because of their effect on tone values, they are corrected automatically, along with all other factors which affect tone values, when the radial distribution of light in the half-tone dots is adjusted, as described in the paper, to produce the required type of tone rendering. Suppose for example that small dots etch shallow, and therefore produce a paler tone than they would with uniform etching depth, the method of correction employed automatically ensures that such dots are made as much larger as is required to compensate for their shallow depth.

MR. S. G. CORBISHLEY: Has the author any comments to make on the value of electrolytic etching for the obtaining of better grading of tone values?

MR. YELLAND: It is sometimes claimed that electrolytic etching produces less sideways spread of the etched recesses than does etching with the customary mordants, for example ferric chloride, when etching to the same depth. If the claim were well-founded it would mean that, in this respect, electrolytic etching might have some advantage over mordant etching from the point of view of control of tone-values.

It appears, however, that in the etching of an etched recess, some attack takes place on all exposed surfaces, i.e. on the sides of the recess as well as the bottom, whether the attack is by mordant, or by electrolysis, so that the difference in effect between the two methods of etching would in general be one of degree only, and might be rather small. Probably, rather larger differences would be produced according to the type of resist layer employed, particularly in respect to the manner in which the resist fringe, left overhanging the rim of the recess, breaks down as etching proceeds.

The influence which the dot-expansion in etching has on the tone-values, is in any case fully taken into account in the method of tone-control described in the present paper. If, for example, any change in etching conditions were made, which had the effect say that larger etched recesses than formerly resulted from a given size of dot in the diapositive film, then the radial distribution of light in the half-tone dots would be correspondingly adjusted to ensure that the dots on the film, which represent any given tone of the original, were automatically made as much smaller as they need to be to restore the required tone in the eventual reproduction on the cloth. The ease and effectiveness of control are, however, improved if the dot-expansion in etching is not too great.

MR. G. WALLER: In view of the lecturer's remarks on the subject of moiré effects from interference between a half-tone screen pattern and the woven fabric it is interesting to note that in the early days of half-tone an irregular pattern of dots was used in Wheeler's metzograph screen. This should lessen the moiré effect considerably. I believe it fell out of use as the regular ruled screen pattern gave less trouble in etching. Has the lecturer any comments on this point?

MR. YELLAND: Since moiré patterns are formed by the super-position of regular structures, it is an attractive idea to try to eliminate them by making one of the structures, for example the screen, irregular. A difficulty arises in that the moiré is not completely eliminated unless the screen is made completely irregular, but complete irregularity is not easy to define or to achieve. For example, even an irregular grain screen must have a certain average number of grains per inch, and the actual grains per inch in any given area (a square inch say) in practice cannot vary outside certain limits without introducing unwanted variations of tone and texture.

A good approximation to the required effect could probably be obtained by the use of screens like Wheeler's Metzograph screen, as suggested by Mr. Waller. These screens did not appear to be commercially obtainable at the time of the experiments described, but screens of a similar type were made by producing a carefully controlled reticulation of a layer of gelatin on a transparent glass plate. The reticulated surface can be made to consist of a network of interlacing curved cylindrical lenses of positive refracting power; the surface thus composed can be used as a half-tone screen in conjunction with a radially graduated light-source like that described in the present paper. In practice, it was found difficult to keep the reticulation of the gelatin surface sufficiently uniform over the whole area of the screen, in point of focal length of the lenses and of the number of lenses per square inch. Thus the precision of control of tone rendering was not so good as could be obtained with screens of regular structure. It is also the case that depending on whether the half-tone is a positive or a negative, the "engraving top" is less regularly formed than from a normal screen, and this does lead to difficulties in etching, as mentioned by Mr. Waller.

Mélange or Vigoureux Printing

F. BUXTORF and A. WIAZMITINOW

This paper describes the equipment and the methods used in the Vigoureux printing process for wool, rayon staple, and polyamide fibre slubbing.

In 1863 patents were granted to Stanislas Vigoureux¹⁻³ for a machine for printing slubbing.

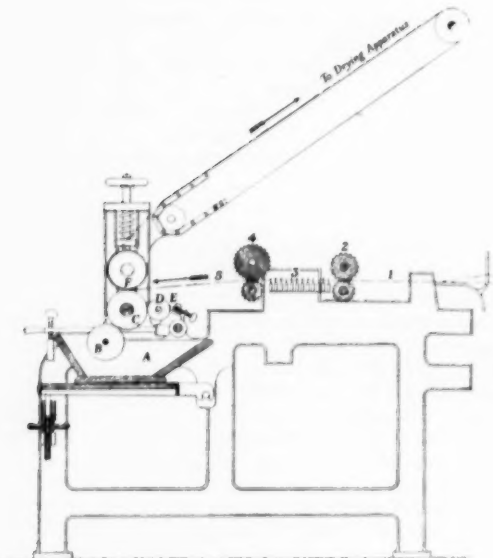
The purpose of this invention can best be illustrated with slubbing or worsted yarn samples. The common method of producing coloured-and-white blended yarns or fabrics is to dye the wool in the slubbing stage and subsequently to blend with a suitable proportion of white before spinning. In all cases where this method of production is used, the resultant fabric has a somewhat streaky appearance, owing to the fact that whole staples of coloured or of white wool tend to be exhibited on the surface of the cloth, and the degree of such streakiness is always governed by the length of staple of the wool which has been dyed. Even when the utmost care is taken by numerous passages through the gillbox, it is still fundamentally impossible to produce really uniform results. By the use of the Vigoureux printing process, however, this defect can be eliminated.

The Vigoureux process consists broadly in printing a wide web of slubbing with diagonal or

lateral stripes of colour, a proportion of the slubbing being left unprinted, so that during subsequent gilling and combing a uniform yarn and finally a uniform coloured-and-white fabric is produced. The overall depth of colour of the final fabric is determined by the area of the slubbing web which is actually covered or printed. A comparison between fabrics produced from Vigoureux-printed slubbing and from dyed-and-white slubbing respectively illustrates these points very clearly, the "sparkle" of the Vigoureux-produced cloth being far preferable.

In the last two or three years the demands of the trade for higher-quality specialities, in both women's and men's worsted suitings and also in flannels, have created a new demand for mixture fabrics of this class, and as a result the process of Vigoureux printing has been given an added impetus.

Fig. 1 reproduces the drawing accompanying the original patent specification¹. The Vigoureux machines now in use do not differ greatly in principle from the original design. Improvements in the gill-box have been made, following the development of spinning machinery, and the mechanical sections of the printing apparatus have been modernised (Fig. 2-4).



- 1 Initial position of wool or other fibrous web
2-4 Construction of gillbox
5 Direction of web

- A Colour trough
B Colour-supply roller
C Roller covered with elastic or porous material
D Doctor or expressing roller
E Scraper
F Engraved printing roller
G Apron or endless cloth for conveying printed web to drying apparatus

FIG. 1—Diagram of Vigoureux Printing Machine¹

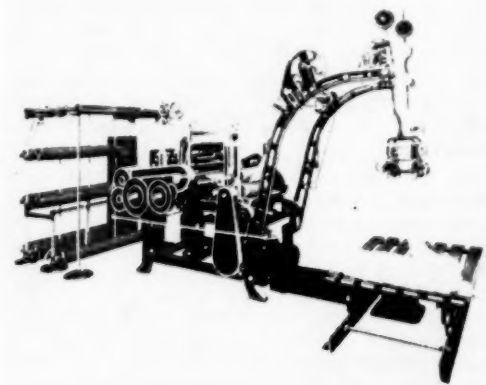


FIG. 2—Mélange Printing Intersecting Gill with Feeding Arrangement

A later patent⁴ provided for the production on the Vigoureux principle of two-colour and multi-colour prints, two printing units being assembled in series. Several other applications were foreseen, but none of these has since gained acceptance.

In more recent times machines with two printing rollers have been manufactured, both of which act on the same colour roller (Fig. 5). The two rollers

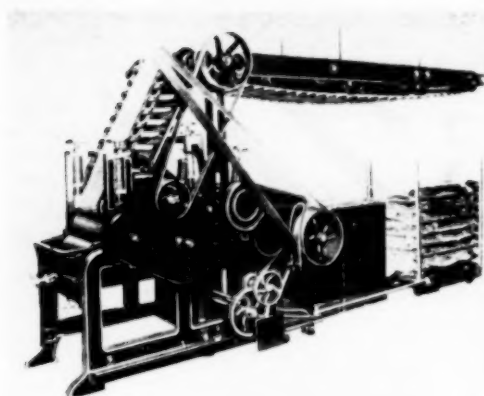


FIG. 3—Mélange Printing Gill with Lattice Delivery

are engraved with alternating spiral ribs. The advantage of this arrangement is that prints can be produced with considerable variation of coverage with a relatively small number of rollers. The Société Alsacienne de Constructions Mécaniques of Mulhouse manufactures rollers in four standard sizes. These give prints covering 18%, 27%, 50%, and 70% respectively of the total surface area, and by combining them as shown in Fig. 6, eight different coverages can be obtained.

WOOL 5-7

In the printing of woollen cloth the wool is normally chlorinated before being printed, but this treatment is totally unsuitable for slubbing to be printed by the Vigoureux process, although it has often been suggested. The reason is, of course, that slubbing printed by this process must possess the same spinning and weaving properties as normal

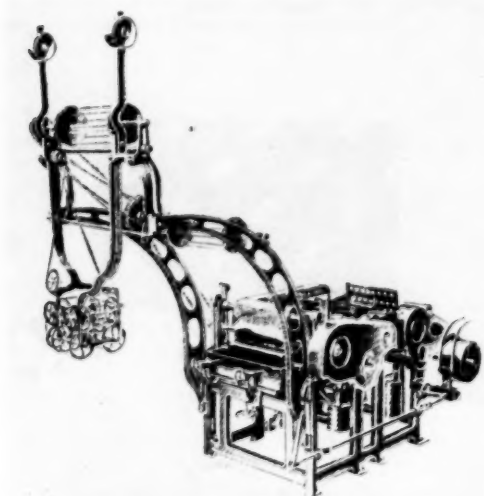


FIG. 4—Vigoureux Gillbox

slubbing, and such chlorinated wool would not be suitable for production of the highest-grade fabrics.

It is essential during the Vigoureux process that good penetration of the slubbing web should be obtained, and for this reason the printing pastes should not be too thick. Before transferring printed slubbing from the Vigoureux machine to the steaming cabinet, it is advisable to allow it to lie for a short while as it is delivered from the machine, so that the printing paste may fully penetrate the wool fibres.

The first requirements of dyes for Vigoureux printing are good working properties, involving good solubility and rapid fixation by the steaming process allowed, and also a high standard of fastness to washing, milling, light, perspiration, and rubbing. The classes of dyes which meet these requirements

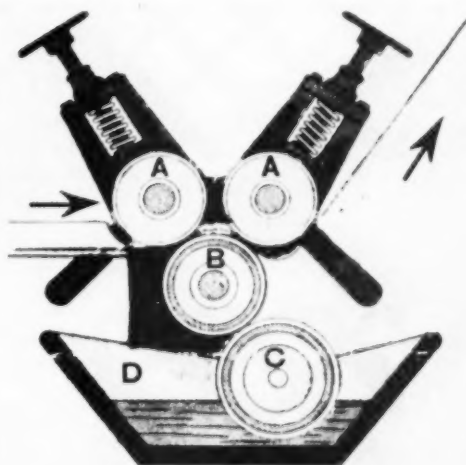


FIG. 5

are the fast-to-milling acid dyes and the more recently introduced metal-complex dyes of the Cibalan (Ciba), Irgalan (Gy), Lanasyne (S), and Neutracyl (DuP) types, and also the afterchrome dyes. Of the latter class, it is necessary to select those members with which development of the chrome lake is most easily effected.

The following recipe (in parts by weight) may be regarded as typical for the acid and the metal-complex dyes—

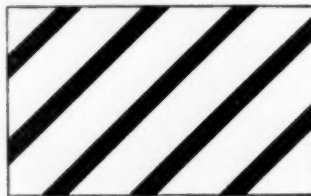
20	Dye
40	Thiodiglycol or pyridine
320	Water
50	Glycerol
500	British gum (1 : 1)
60	Ammonium tartrate
10	Sodium chloride

1000

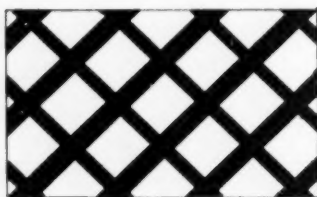
Thiodiglycol, pyridine, and water act as solvents; glycerol keeps the slubbing moist, and prevents it from drying out before steaming; while British-gum thickener can be replaced in the case of acid



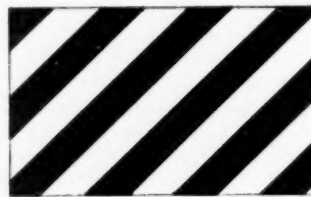
Roller No. 1—18%
(printed bars running to the left)



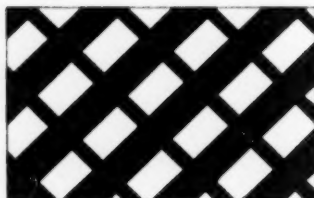
Roller No. 2—27%
(printed bars running to the right)



Rollers No. 1 and 2—40%



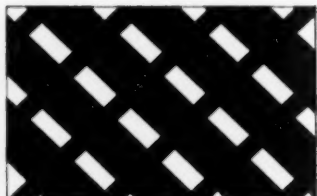
Roller No. 3—50%
(printed bars running to the right)



Rollers No. 1 and 3—60%



Roller No. 4—70%
(printed bars running to the left)



Rollers No. 2 and 4—78%



Rollers No. 3 and 4—85%

Direction of the wool after printing

FIG. 6—Percentages of the Surface Area printed

dyes by Sennar gum, dextrin, tragacanth, etc. Ammonium tartrate or oxalate, and oxalic acid where suitable, are used with acid dyes for fixation. Sodium chlorate prevents any reducing action either by the fibre or by the thickener during steaming. The addition of an agent to counteract foaming has proved of value for dyes having this tendency.

The following is a typical recipe for chrome dyes—

30	Dye	
40	Ammonia (25%), thiodiglycol, or pyridine	
190	Water	
50	Glycerol	
500	British gum (1 : 1)	
20	Ammonium oxalate	
30	Chromium fluoride, $\text{CrF}_3 \cdot 4\text{H}_2\text{O}$	} Heat to dissolve
130	Water	
10	Sodium chlorate	
1000		

Ammonium oxalate and oxalic acid act as fixing agents; British gum and certain lichenous preparations, marketed under the name *Sennar gum*, as thickeners; and chromic fluoride, formate, and acetate as chrome mordants. Similar recipes and details of the most suitable solvents can be found in the pattern-cards issued by dye manufacturers.

In bulk practice there are two methods for preparing the printing paste. Sometimes a stock solution is prepared from the dye, the solvents, glycerol, and British gum, and the other chemicals are mixed into this shortly before printing. This procedure has the advantage that larger quantities of stock colour can be stored at one and the same time, but the drawback is that the tinctorial power does not remain constant when the solution has been standing for some time, even after thorough stirring. Other printers prefer to make up the paste separately for each run, to make sure of getting a consistent shade.

Normally, for printing, sixteen tops of slubbing are mounted on the creel, and from each of these tops a sliver of about $\frac{1}{4}$ oz./yd. average weight is run through the gillbox attached to the machine, which usually has a draft of 1 : 4. A web 12–20 in. in width, weighing approx. 3 oz./yd., is delivered from this gillbox and passed between the printing and the colour rollers.

The colour roller, made nowadays of metal covered with wool felt, is impregnated with print paste from a rubber roller rotating in the trough. The printing roller is of bronze and is engraved with raised spiral or lateral ribs.

The web is thereby impregnated with the print paste as the raised surfaces of the printing roller or rollers exert pressure on it. The printed slubbing is then conveyed by a mechanical folding device on to metal trays or cages standing on a lattice which has a lateral traverse (Fig. 2 and 4).

The colour is fixed on the wool by steaming, but, as previously mentioned, it is always advisable to allow the slubbing to lie for a short time before the batch is actually conveyed to the steaming cabinet. It is important, however, that the colour should not dry into the slubbing, otherwise difficulty will be

experienced in obtaining full development of the shade. Steaming is usually carried out for two separate periods of 1–1½ hr. each with damp non-pressurised steam, and the slubbing should be allowed time to cool between the two steaming operations. Fast-to-milling acid dyes and dyes of the metal-complex types previously referred to require only one steaming to attain their full fastness properties.

After being steamed, the wool is passed through the backwashing machine, and for thorough and complete removal of surplus dye, thickener, etc. it is desirable to use four- or five-bowl machines for this purpose. The backwashing machine provides for subsequent drying and also for the first gilling operation in the gillbox which is attached to the drying section of the backwashing machine.

Before being passed to the spinners, the wool is gilled several times and matched to shade in the form of a small felt pattern.

It is desirable that slubbing for Vigoureux printing should not be of too high a pH value, and generally speaking 8.5 should be considered the maximum. The reason for this is that higher pH values would tend to produce yellowing of the white during steaming. For similar reasons, it is not desirable to use an alkaline soap in the backwashing machine, a synthetic detergent being preferable.

The oil content of the slubbing as delivered to the Vigoureux printing machine is also important: too high an oil content tends to give prints with poor rubbing fastness. On the Continent, dry-combed tops are frequently used where Vigoureux printing is to be undertaken.

RAYON STAPLE⁸

The same process has been adopted for rayon staple, both during and since the 1939–1945 war, to meet the demand for Vigoureux-printed tropical suitings and women's dress goods. As in the case of wool, the properties needed here are good to very good fastness to light, washing, milling, and perspiration.

There are several classes of dyes which are suitable for vegetable fibres. First among these are the mordant dyes, mostly anthraquinone derivatives, which are applicable both to pure rayon and to wool-rayon mixtures. For faster colours the sulphuric esters of the leuco vat dyes are the outstanding group, marketed under the proprietary names Indigosol (DH), Anthrasol (DH), Sandozol (S), Cibantine (Ciba), Tinosol (Gy), and Soledon (ICI).

The following printing recipe is an example of those used for the leuco vat class of dyes—

40–80	Dye
20–80	Thiodiglycol or urea
630–340	Hot water
250–400	Thickener
40–80	Sodium nitrite soln. (33%)
20–20	Soda ash soln. (10%)
1000	

Without being dried, the material is steamed for 30 min. in the usual type of steamer and developed at 40–70°C. (105–160°F.), according to the dye used,

with 20 c.c. sulphuric acid (168° Tw. or 66° Bé.) per litre of water, to which 1–2 g. sodium nitrite and 2–5 g. urea per litre have been added. It is then rinsed in warm and in cold water, neutralised with a little soda or ammonia, and dried. Development in an acid bath is completed in 8–12 sec. It is often possible to develop without sodium nitrite and urea; this can be ascertained by preliminary trials.

For deep reds, bordeaux, browns, and blues, prepared printing colours containing diazotised and stabilised bases together with azoic coupling components can be used. These products are sold under the trade names Rapidogen (IG), Brentogen (ICI), Cibacogen (Ciba), and Sandogen (S). A suitable recipe is—

50–80	Dye, pasted and dissolved in —
30–40	Caustic soda (32%)
30–30	Alcohol
200–200	Water

This solution is stirred into —

300–400	Neutral thickener, and
390–250	Water is added to bring to —

1000

Without being dried, the material is steamed for 10–20 min. in equipment suitable for acid steaming, then washed, soaped at 60°C. (140°F.), rinsed, and dried.

Vat dyes can be used for rayon printing, but with the kind of steaming equipment commonly used for Vigoureux work it is seldom possible to carry out steaming under completely airtight conditions.

Less complicated methods are needed for the sulphur dyes—

PRINTING RECIPE

15–50	Sulphur dye
60–60	Glycerol
100–100	Glucose
250–250	LS soln. (see below)
40–40	Hydrosulphite RFN (1 : 1)
450–450	British gum (1 : 1)
85–50	Water

1000

LS SOLUTION

110	Caustic soda (72° Tw., 38° Bé.)
30	Soda ash, dissolved in —
110	Hot (200°F.) water

250

Print and, without intermediate drying, steam for 20 min. The steam should be saturated and free from air. After being steamed, the slubbing is oxidised in a bath at 50–60°C. (120–140°F.), given a cold rinse and a warm soaping, then rinsed a second time, and finished.

Prof. J. B. SPEAKMAN: Fabric produced from mélanged slubbing is, of course, much more uniform in appearance than one containing coloured fibres and uncoloured fibres, but the authors' statement that "a uniform coloured-and-white fabric is produced" by mélanging is an

OXIDISING BATH

2 g. Sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ } per litre
40 g. Acetic acid (9° Tw., 6° Bé.) } of soln.

The Cuprofix (S) dyes are applied by a simple method that gives very fast-to-light prints with good wet fastness properties in the majority of cases. A typical recipe for this class is as follows—

10–30	Dye
30–50	Thiodiglycol
120–120	Urea
335–245	Hot (200°F.) water
450–450	Tragacanth (6%)
15–150	Sodium phosphate
30–30	Wetting agent
10–10	Sodium chlorate

1000

Print, steam for 60 min., rinse, treat in another section of the backwasher with 7–10 g. Cuprofix Salt per litre for 60–80 sec. at 80°C. (175°F.), and then give a final rinse.

POLYAMIDE FIBRES

In recent years the Vigoureux method has been used also for polyamide fibres, chiefly for blending in tropical suitings. The fast-to-milling acid dyes are the most important class here, followed by the new chrome-complex dyes of the Cibalan, Irgalan, Lanasyne, and Neutracyl types, and chrome dyes that are easily developed.

A typical recipe for acid dyes is the following—

30	Dye
100	Thiodiglycol
450	Hot (200°F.) water
300	Industrial gum (1 : 1)
60	Thiourea
60	Ammonium tartrate (1 : 2)

1000

* * *

The great importance that is attached to the Vigoureux method in the industry today is due less to improvements in the process or to more rational working methods than to the dictates of fashion. In fact, the present demand for even shades on many kinds of material can be satisfied only by this printing method.

SANDOZ LTD.

BASLE

SWITZERLAND

(MS. received 17th June 1953)

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Discussion

exaggeration. The statistical aspects of mixing have not been given sufficient weight. From this point of view, the merits of mélanging may be summarised as follows: no matter how often mixtures of coloured and white fibres are re-combed, it is impossible to prevent some grouping of

coloured fibres and of white fibres, and the appearance of the resulting yarn and fabric is uneven. Similarly, when each fibre has coloured and white parts, it is impossible to prevent the grouping of coloured sections and uncoloured sections. But whereas there is, so to speak, "three-dimensional unevenness" with mixtures of coloured fibres and white fibres, there is only "two-dimensional unevenness" with fibres which all have coloured and white regions, and the fabric made from mélangé slubbing is the more uniform in appearance. It is not, however, free from the unevenness due to the grouping of coloured regions and white regions of different fibres, though the unevenness is far less than with mixtures of coloured fibres and white fibres.

Dr. BUXTORE: It is true that an absolutely uniformly coloured and white fabric is not produced by the normal Vigoureux process but the slight inequality is of little practical importance. It could be completely eliminated by printing the stripes much closer together, but this would, to some extent lessen the mélangé effect of the final cloth.

Mr. H. A. TURNER: While we must agree with Professor Speakman that the difference in the efficiency with which mixing takes place with, respectively, the blending and the Vigoureux methods is essentially a problem of statistics, it seems to me that the qualitative answer is sufficient to determine what will happen in practice. In blending, to ensure that the hair in a sliver of one colour is removed from among its fellows and is placed against a hair of a second colour, it must be selected as an individual and moved bodily to some other grouping of fibres. In a printed sliver each fibre may retain its neighbour and requires only a displacement of a fraction of an inch in the direction of its length—essentially a drawing action—to ensure that its coloured regions do not coincide with the same regions on its neighbours. It would appear that colour coincidence in adjacent hairs is overwhelmingly less probable in the latter event. While considering mixing as a problem in statistics, one may be permitted to ask why the mélangé printers use the customary simple rhythmic patterns of which examples are given. Would not the probability of colour coincidence be reduced almost to zero if irregular patches of colour were printed on?

Dr. BUXTORE: In practice it would be found that the more regular the printing, as used at present, the more complete the blending of coloured and white in the final cloth. If irregular blotches were printed the tendency would be to give more irregularity finally as is given by blending coloured and white fibres.

The perfect uniformity of appearance obtained by the Vigoureux method is due not only to the drawing operation but also to the several doubling processes which occur throughout the whole preparation of the wool before spinning.

Mr. F. SMITH: What is the best temperature and humidity for steaming?

Dr. BUXTORE: The steam used is at atmospheric pressure with humidity as high as possible.

Mr. SMITH: Also why do you get a colour halo in printing blacks. Is it possible to prevent it?

Dr. BUXTORE: This effect is due to the mechanical arrangements for printing in the Vigoureux process by which it is not possible to get the sharp outlines obtained in calico printing, but as thorough mixing takes place by regilling after printing this is of no importance.

Mr. F. CROMPTON: Is any mélangé printing done on cotton?

Dr. BUXTORE: As far as we are aware mélangé printing is never carried out on cotton.

Mr. A. H. WYLD: Why, with chrome dyes, is it necessary to steam for two successive periods of one hour each interposed with a conditioning period also of approximately one hour rather than a straight two hour steam?

Dr. BUXTORE: It has been found by bulk experience that interrupting the steaming process as given in the paper does produce a better result, e.g. better colour yield, than would be given by an uninterrupted steaming for the same period, but the theoretical reason for this is not known.

For neutral dyeing Acid and metal-complex wool dyes a single steaming period of one hour is sufficient.

Mr. WYLD: The gradual wearing of the felt on the felt-covered roller gives rise to difficulties in that the reduced absorbency of the felt means that less colour is transferred to the slubbing web, giving rise to a weaker shade. Can the speaker recommend any special quality of felt or alternatively has he any experience of its replacement with a rubber-covered roller with a semi-porous surface?

Dr. BUXTORE: A specially manufactured felt for this roller is used and we do not know of any other material which could be employed. The difficulty of reduced absorbency of the felt can be overcome by control of the uptake of the dyestuff, as mentioned in the answer to Mr. Russell, by adjusting the pressure between rollers B and C (Fig. 5).

Mr. N. W. YELLAND: Does Fig. 6 represent actual size of engraved pattern?

Dr. BUXTORE: Fig. 6 does not represent the actual size of the prints, but is drawn to scale, the actual distance from one edge of a stripe to the corresponding edge of the next stripe is approximately one inch.

Mr. YELLAND: Is size of pattern adjusted according to staple length of fibre?

Dr. BUXTORE: No alteration of this kind is made.

Mr. J. STARKIE: Does the presence of oil in the slubbing have any effect on the uptake of the colour?

Dr. BUXTORE: Our experience is that a dry combed top in general gives a deeper shade than a top in oil.

Mr. A. S. FERN: To obtain a typical grey mélangé fabric, what are the relative amounts of dye required to give the same visual effect in the finished piece—

- (a) when the slubbing is mélangé-printed and
- (b) when black and white slubbing is blended?

Dr. BUXTORF: Exact comparisons of the amount of dye required are not available, but it can be stated that the amount of dye needed in the mélange process is greater than would be required to produce a similar effect using dyed and blended slubbing.

Mr. FERN: What is the light fastness of the fabrics obtained by methods (a) and (b) above?

Dr. BUXTORF: The light fastness given by the two methods is the same. From time to time one difficulty occurs, i.e. when a Grey is printed with a Chrome Black. It is not always realised that whereas a Chrome Black is very fast to light as a Black it is not necessarily so as a light Grey. For such purposes a neutral dyeing metal-complex or a chrome Grey should be used.

Dr. VICKERSTAFF: With regard to Mr. Fern's question, it must be observed that mélange printing is inherently an inefficient method of producing grey shades insofar as dye usage is concerned. The aim in this type of work is to produce a heavy black in the printed areas so that the contrast between printed and unprinted fibres, which gives the characteristic sparkle of mélange fabrics, is retained. Consequently the light absorption of the printed areas is very high and the over-all reflectance of a grey mélange fabric is determined largely by the ratio of coloured to uncoloured areas in the initial printing. If, for the purpose of illustration, it is assumed that dye equivalent to a 10% shade is applied to the printed fibres and that the reflectance of these fibres is say 5% of that of the unprinted fibres, then rough calculations indicate that in a grey produced by printing 20% of the total area (and having a reflectance of about 80%) an equivalent shade could be produced by straight dyeing with only half to one-third of the amount of dyestuff employed in the mélange fabric. Naturally, this disadvantage becomes less pronounced as the printed area increases (i.e. as the greys become darker in shade) and the two methods of colouration must give the same result at 100% coverage.

On the question of fastness, it might be expected on theoretical grounds, since light fastness is known to increase with increasing depth of shade, that the light fastness of mélange greys would be higher than the equivalent dyed greys. There is more dyestuff to be destroyed in the mélange fabric. Whether this effect is observed in practice I do not know.

Mr. F. SMITH: In weaving printed yarns printed in even sections one can get irregular patterns formed that are not repeatable; one copy will give one design, the next will give another,

giving a barry effect to a woven or knitted fibre. Is it not possible then that the coloured part of the sliver can at times draw alongside the coloured and the white against white thus defeating the ends of mélange printing, if only regilling is done and not recombining.

Dr. BUXTORF: It is true that in Vigoureux printing some unevenness can occur, but as the gilling process which follows printing intimately mixes the individual fibres the effect is always much more even than the result which can be obtained by blending. If recombining is also possible, the chance of barriness is practically eliminated.

Mr. G. WALLER: In the lecture and discussion so far the question of printing more than one colour to get additional effects has not been raised. Is this because difficulties of production are too great or because there is no demand for it anyway, either now or in the future?

Dr. BUXTORF: A printing machine to print two colours was patented by A. Benn in 1880, and did consist of two different printing arrangements, one behind the other, but no developments of this kind have taken place to our knowledge. A method that is sometimes adopted is to dye the slubbing first and then to overprint.

Mr. A. N. RUSSELL: In mélange printing, how do you match to a shade in practice?

Dr. BUXTORF: There is no laboratory-size Vigoureux printing machine and the nearest approximation in the laboratory is a kind of block or screen printing. In this case the uptake of the print paste by the wool is not controllable, so that the recipe is not reproducible in bulk. A recipe for Vigoureux printing can therefore be worked out only on the full scale machine.

The printing machine itself can introduce unevenness, caused by—

1. the age of the felt on Roller B in Fig. 5;
2. the pressure on the Roller A in Fig. 5;
3. the pressure between Rollers B and C in Fig. 5.

Such inequalities can be overcome by controlling the uptake of the print paste, by suitably adjusting the machine, to a percentage, calculated on the weight of the slubbing, equal to the percentage coverage required. In other words slubbing printed with 50% coverage should have an average uptake of print paste equal to 50% of the weight of the slubbing.

Printed slubbing is matched in a similar manner to dyed slubbing. The whole quantity is not printed at once, but in different batches, and one batch is blended with the other to produce the desired shade.

The Production of Metal Screens

G. WALLER

A new method of producing printing screens from metal is described. Although the method requires a higher degree of technical skill and additional capital outlay compared with normal methods, improved results are obtainable in the life and accuracy of registration of screens, and in addition it is possible to gain greater control over the quality of printing by variation of the screen mesh.

INTRODUCTION

Hitherto the universal practice in screen-making has been to start with a woven fabric, usually of silk or other textile fibre, less commonly of bronze metal, and fill in the interstices with lacquer in the parts which are not required to print. The portions of the screen remaining in the open woven state form the printed pattern. Attempts have been made to produce screens which are more resistant to printing, by the use of more resistant materials for filling the woven mesh. In the case of metal screens, metal has been deposited in the mesh; thus, according to one patent¹, the mesh is first filled with a film of a different metal which can be etched away without the woven ground being etched. Nevertheless, all these methods produce screens which still consist of the basic woven fabric.

By taking as the starting point a thin sheet of metal such as copper, and etching through in an appropriate pattern, a screen is produced which is not only more resistant to print colours, but in which much greater control is possible over the form of the basic mesh.

METHOD OF PRODUCTION

In principle the screen is made by a similar method to that by which line and half-tone process blocks are made for letterpress printing, except that, by using thin sheet metal and prolonging the etching, the pattern is etched through to the back of the plate.

Initially a positive transparency of the design is made by the usual methods of copying the design, either photographically or by tracing by hand; this consists of solid opaque areas (in the parts required to print) on a transparent ground. It is usually sufficient at this stage to draw a single "repeat" of the pattern. It is then necessary to divide the solid areas into innumerable small dots to obtain the necessary mesh structure, and this can be done either on the positive or during transference of the pattern from positive to metal sheet. The former is more satisfactory and gives more control over the mesh used.

To obtain a dotted positive it is merely necessary to produce a contact negative from the solid positive and then mount this negative with a ruled screen and rephotograph. In order to obtain better printing where a screen pattern is made of fine line work and large areas on the same screen, it is possible at this stage to apply different meshes to different parts of the screen. In this way both fine and heavy parts of the design can be printed from one screen instead of the two that are usually necessary. Throughout this photographic part of the work, of course, it is absolutely essential to maintain perfect contact between negative and

film to avoid loss of sharpness, and a good contact exposing frame, preferably of the vacuum type, is necessary. It is also imperative to keep perfectly clean working conditions, since, as the pattern becomes divided into smaller dots, any corrective handwork becomes increasingly difficult.

As an alternative to making a dotted positive, the solid positive may be used to transfer the pattern to the metal sheet and the dotted effect also applied to the sheet by a separate exposure through a dotted screen. This dotted screen would be a "negative" of the ruled screen which was used in making the dotted positive.

FORM OF MESH

Considerable variety is possible in the choice of ruled screen for producing the dotted positive. The use of the word "ruled" is possibly somewhat misleading here, since ruling is not imperative and a random arrangement of dots, as in the Erwin screen, is satisfactory as long as the dots are separate and reasonably uniform. The term "ruled screen" is used, however, as this probably best conveys the idea required, we have in our trials used mostly a copy on film of a normal ruled screen as used for half-tone process work. The angle of 90° between the two sets of ruled lines is not ideal, as it is found that with fine rulings a square dot etches out more or less circular, owing to less effective etching in the corners of the square. If rounder dots are used in the positive, as in a honeycomb, this non-etching of corners does not occur so much, and a greater proportion of open metal is obtained for the same width of metal ties. At the same time more dots per unit area are obtained. A Schultz screen in which the rulings are inclined at 60° would give this increased number of dots, but the dots would be oval and not round, and the thickness of metal between the open dots would not be so uniform.

In any case, where a screen is used in which the dots are arranged in straight lines, it is recommended that these lines be inclined to the directions of warp and weft of the fabric to avoid interference effects. A more solid print will then result.

METAL SHEET

The choice of metal for this process depends upon individual requirements and the economic factors involved in its supply. The essential properties of the metal sheet are the right thickness and absolute uniformity. The thickness depends largely on the type of pattern which has to be printed, since this influences the size of mesh required. Thinner sheet is required for a fine mesh than for a coarse one, but in any case for ordinary printing a thickness of 0.005 in. is comparable with a silk screen as

normally used. In this work 5-mil (0.005-in.) copper sheet has been used as a standard material.

The main difficulties of the process arise from the thinness and the flexibility of the metal sheet. For level results not only must the thickness be uniform but also the sheet must be perfectly flat and without the slightest sign of kinks or dings. It is advisable to mount the plate on a rigid temporary support at the beginning of the process.

TRANSFER OF DESIGN TO METAL

The copper sheet in its normal state is coated with oxide or other impurities from the atmosphere, and requires scouring with water and fine pumice powder to give a clean surface. To prevent further oxidation the sheet after cleaning is kept covered with water until the photosensitive layer is applied. This process is best carried out on a centrifugal "whirler", so that, after scouring, the pumice may be washed off with running water and the sheet coated without further handling. Thus the copper sheet is fixed on the plate of the whirler and scrubbed with water and pumice by hand. The whirler is then made to rotate slowly (about 60 r.p.m.) and water is poured over the centre. This washes the pumice outwards and off the plate. The coating solution is then poured into the centre and replaces the remaining water. A second application of coating solution is poured on to ensure complete removal of water. The coating is then dried on the whirler by a draught of warm air (not over 40°C.) in subdued non-actinic light.

We have found the enamel process to give the best resistance to etching. The coating solution is made up as follows—

SOLUTION A			
Photoengraver's glue	8 oz.	
Water	7 oz.	
SOLUTION B			
Ammonium dichromate	1 oz.	
Water	4 oz.	

Mix A and B and allow to stand until any sediment has settled. Decant the clear liquid and filter through cotton-wool.

The above recipe can be varied according to working conditions. Addition of ammonia will improve keeping qualities somewhat. Replacement of ammonium dichromate by potassium dichromate increases exposure time slightly. The amount of water used may be altered to give the best thickness of coating, which should be thick enough to form an adequate resist to etching but thin enough to be exposed right through. Usually a thickness of about 1 mm. when wet is adequate.

The coated sheet is now exposed to the arc lamp behind the positive in order to harden the glue behind the clear portions of the latter. Perfect contact between the two is essential at this stage, and for any but the very smallest sizes a vacuum printing frame is necessary. While there is reasonable latitude in the exposure time, this should be standardised and checked each time with a light-meter, as variation in supply voltage to the arc lamp can cause quite a large alteration in the light intensity. With a 50-amp. arc lamp at a distance of

2 ft. the exposure time is of the order of 5–10 min., and should be determined empirically.

The glue which has not been exposed to light is now washed out in cold water, and the remaining, hardened glue, forming the pattern in negative, can be dyed with Methyl Violet in water to render it more visible. The plate is then dried as before with warm air and is ready for burning-in and etching.

"BURNING-IN" AND ETCHING

The plate must now be removed from its temporary support in order to be heated over a gas burner. Heating must be carried out gently and evenly to bake the glue layer into a resistant enamel. On first being heated the dark colour of Methyl Violet disappears, and later the enamel assumes a brownish colour. Heating is continued until a uniform chestnut-brown colour is obtained. Before etching is commenced it is necessary to protect the back and edges of the plate by painting over with an acid-resisting lacquer. At the same time any blemishes on the face, such as are caused by dust specks or bubbles in the glue coating, are corrected.

Two alternative means of etching are possible—(a) with ferric chloride and hydrochloric acid, or (b) electrolytically.

(a) Acid etching is carried out in an earthenware tray, which is equipped with a rocking mechanism and in which the copper plate is immersed in a strong solution of ferric chloride of 36–40° Bé. (i.e. of sp.gr. 1.3–1.4). A certain amount of free acid is present owing to hydrolysis and is controlled by adjusting the strength of the bath initially, and as the bath is used, by small additions of hydrochloric acid. As the bath is used its copper content increases to a point at which etching is slowed down too far and a new bath is necessary. Further addition of acid beyond this point would serve only to loosen the enamel layer, which of course would ruin the plate.

(b) Electrolytic etching, in addition to being cleaner and more easily controlled, has the advantage that the attack on the metal takes place much more in the direction through the plate than with acid. In this case the plate is immersed in a strong solution of sodium and ammonium chlorides, face down on a flat steel plate. The latter is made the cathode and the copper plate the anode with a voltage of up to 10 v. according to the speed of etching required. Copper is removed from the exposed portions of the plate and deposited loosely on the cathode, from where it is removed by periodical cleaning. Evenness of etching is assisted by blowing jets of air into the electrolyte towards the face of the plate.

In both cases etching is continued until the pattern is etched evenly through to the back of the plate. The acid-resisting lacquer is then cleaned off with solvent, and the screen is now ready for re-mounting in a frame and printing as usual.

CONCLUSION

Some disadvantages of this method of screen production are apparent. Firstly, the inherent lack of the elastic stretch and regain present in silk, which gives better registration with metal screens, also makes metal more susceptible to damage by

dinging, i.e. less liable to recover from accidental strain. Greater care is necessary, therefore, in the day-to-day handling of the screens. Secondly, it is virtually impossible to carry out additions to the engraving once the screen is made, so that more care and skill are needed during production to avoid accidental engraving errors.

Against these disadvantages must be set the greater wear resistance of metal screens, which makes this method particularly suitable for printing long runs. Also, there is less danger of attack on the screen by the organic solvents used in the newer pigment printing colours, etc.

Finally, it should be noted that a reversal of this method could be used, so that a screen is built up by deposition of metal on a suitable temporary support,

but this has not yet been fully investigated, as it appears to involve additional steps in preparing the temporary support. As a fresh support would be needed for each screen, this makes the whole process rather too elaborate for practical uses.

* * *

The author's thanks are due to Messrs. James Harcastle & Co. Ltd. for permission to publish this paper.

JAMES HARCASTLE & CO. LTD.
BRADSHAW WORKS
NEAR BOLTON
LANCASHIRE

(MS. received 20th May 1953)

Reference

¹ Brennan, J. B., and Marsh, E. L., *USP* 2,395,448 (1946).

Discussion

Mr. N. HAMER: In view of the ease with which metal screens can be damaged, has any difficulty been encountered in cleaning?

Mr. WALLER: No difficulty has been met in cleaning metal screens, as against silk screens. Care is necessary to avoid dinges, but if any brushing is necessary in cleaning this can be done by laying the screen on a flat table to form a solid support.

Mr. HAMER: In preparing the screens, is there any tendency for the glue to chip off in the "Burning-in" process, and would there be any advantage in using an electric hot-plate instead of the bunsen mentioned in the text?

Mr. WALLER: There is a tendency for the glue to chip off if it is not applied evenly, or if the exposure, or the thickness of the coating, is not correct.

Any method of heating may be used provided that it is even; gas appears to be most common in the engraving trade.

Mr. HAMER: The lecturer has pointed out the need for greater care in handling metal screens. Has he experienced any difficulties under works conditions, in avoiding damage?

Mr. K. LOWIT: Metal gauze screens are sensitive to careless handling in the print shop. What are your experiences in this respect with the metal sheet screens?

Mr. WALLER: The question of avoiding damage to metal screens is present no matter how the metal screens are made. It is equally important in the use of silk screens, and so should present no added difficulties to anyone used to handling screens.

Mr. LOWIT: What is the finest photoscreen which you can use when making metal screens?

Mr. WALLER: Up to the present we have not gone finer than 70 lines per inch.

Mr. W. B. MILLER: Has the author engraved a full design and done a production run or is he merely speaking of experimental work?

Mr. G. WALLER: The work has so far been experimental, but small screens have been made of handkerchief size to test under actual printing conditions. Further trials are proceeding.

Mr. J. H. FLEMING: Since designs for screen printing are usually produced for a limited yard-

age, the economies of any new process for screen products demand careful consideration.

Has this aspect been considered, and if so can the speaker give some indication of relative costs?

Mr. WALLER: The question of economics has only been gone into briefly, but so far it appears that materials will be reasonably cheap while skilled labour and equipment may cost more than for silk screens.

In view of the greater durability of metal, this method will be more useful in the case of longer runs, or in conjunction with automatic screen-printing machines.

Mr. W. A. FALCONER: What influenced the author to select 0.005 in. as the thickness of copper sheet? Can a thicker sheet be used and if so what is the maximum thickness which can be used and still obtain a satisfactory through etch?

Mr. WALLER: A thickness of 0.005 in. was chosen as this is about the thickness of a normal silk screen, and would be expected to give similar printing behaviour. The thickness is influenced by the size of hole which it is desired to etch through. As the thickness of the sheet is increased, so must the minimum size of aperture be increased as well.

In brief, the limiting factors are the fineness of the design on the one hand, and the weight of colour to be printed on the other.

Dr. A. E. STUBBS: In view of the high susceptibility of copper sheet to mechanical damage, has the lecturer tried the use of metals of appreciably higher elastic limit, such as phosphor bronze or even spring steel, which may be subsequently plated if desired?

Mr. WALLER: Up to the present our trials have been confined almost entirely to copper sheet, as this is more readily available in the required thickness, and also was expected to have better etching properties than, for example, spring steel. Phosphor bronze has been used also without difficulty.

Mr. R. THORNTON: The use of this technique would imply that the greater accuracy expected from all metal screens would make them very suitable for mechanised screen printing equipment. Does the planished metal under-surface pick up

more or less colour when in contact with a wet print?

Mr. WALLER: We find that the under-surface of a metal screen produced by this method is very similar, as regards smoothness of surface, to a normal silk screen, which is of course, completely filled, in the non-printing portions, with screen lacquer.

Mr. THORNTON: Are such metal plates more or less liable to show up frame distortion than mesh screens?

Mr. WALLER: Metal screens, being less elastic than silk, are under less tension on the frame and consequently both the frame and the pattern are less liable to suffer from distortion.

Mr. C. W. SEELEY: Are the frames which are used in connection with the planished metal screens of wood or metal?

Mr. WALLER: Wooden frames have been used up to the present. Since the metal screen is not required to be held under tension to the same extent as a silk screen, the major objection to wood does not apply.

Mr. SEELEY: By what method is the metal sheet secured to the frame?

Mr. WALLER: The metal sheet is secured to the wooden frame by tacking, the tacks being covered by adhesive tape to seal the joint between metal and wood.

THURSDAY MORNING, 24th SEPTEMBER 1953

Chairman — G. S. HIBBERT, Esq.

Doctor Streaks—Their Origin and Prevention

EMIL A. KRÄHENBÜHL

Based upon the theory that excessive friction between doctor blade and roller surface is the primary cause of roller damage and can provoke this trouble even in print pastes containing no trace of solid matter, the author reports on trials with a printing assembly linked with a friction-measuring device. The entirely different behaviour of thickenings with high and others with low dry content gives evidence of their varying working properties. It is shown that the use of thickenings with high dry content, addition of lubricants to print pastes containing low dry content thickenings, and especially replacement of copper rollers by chromium-plated ones, will in most cases eliminate the causes of roller damage. There is, however, an indication that changes of pH may completely alter the friction characteristics of thickenings and that with more and more ingredients present in the print pastes their performance becomes increasingly unpredictable and requires closer investigation.

The well known and troublesome defect of doctor streaks in roller printing is generally believed to originate from hard particles—sand, grit, salt crystals, etc.—in the printing paste. These are trapped under the doctor, and scratch the surface of the copper roller or even cut through the edge of the steel blade, thus causing faulty prints.

What appears to be the obvious method of overcoming this fault is to strain the colours through a tightly woven cotton cloth and to ensure that the staff use sand-free tap water to clean the rollers, doctors, and colour boxes. In reality, however, despite strict supervision of all operations and odd jobs connected with the printing process, the author experienced such serious trouble from this source that he decided to investigate the matter more closely.

It often happened that a printing paste containing no solid matter at all ran only a few hundred yards and then began to scratch the roller surface so badly that the machine had to be stopped, and the roller removed and repaired. During the preparation of the paste every ingredient had been carefully dissolved and added to a normally prepared thickening such as tragacanth or starch—tragacanth, and the whole strained twice through a percale cloth. When the machine was stopped and the colour examined, nothing but small copper particles were found. These were undoubtedly the hard particles with a grinding action. They had obviously been torn from the roller surface, but the problem was to find out what had caused the initial damage.

The author then remembered an observation which he had made about twenty years earlier and which had induced him to attribute this phenomenon to excessive friction between roller surface and doctor blade. Copper is a metal with more pronounced ductility than elasticity. The position of the doctor blade with its continual tangential impact upon the roller has a deforming action on the copper crystallites situated on the surface. They are drawn lengthwise to such an extent that, if the strain becomes too great, the tip of such a crystallite eventually breaks, leaving behind a tiny hole. This will rarely be observed, but the copper particle, immersed in the printing paste, will sooner or later become trapped under the doctor and exert its deleterious grinding action.

If this theory is correct, any measure which will reduce the friction between roller surface and doctor blade should help to prevent doctor streaks—

- (i) Lowering of the weights on the levers of the doctor
- (ii) Reduction of the speed of the machine
- (iii) Addition of lubricants to the printing paste
- (iv) Replacement of a thickening of low dry content by others of high dry content
- (v) Homogenisation or mill-grinding of printing pastes
- (vi) Replacement of the steel blade of the doctor by a brass one
- (vii) Replacement of the copper by chromium-plated rollers.

And, indeed, all this helped. Naturally, not all these changes were equally welcome. For example, (i) and (vi) increased the danger of flushing; (ii) slowed down production; and (iv) was not always possible, e.g. with diazotised bases on naphthol prepare or aniline black. But there still remained (iii), (v), and (vii), of which (vii) is undoubtedly the most effective. Unfortunately, the author was then unable to have his rollers chromium-plated, but by using special thickenings, grinding down obstinate colours, and adding suitable lubricants, he was able to eliminate this trouble almost completely.

A paper on this subject¹ in 1941 passed unnoticed, but when invited to present a paper at this Symposium, I attempted to obtain experimental data in support of the above theory.

APPARATUS

The apparatus shown in Fig. 1 represents a printing unit and comprises the printing roller of a laboratory printing machine, 8½ in. wide and 11½ in. in circumference, driven by a motor with adjustable speed varying from 0 to 120 r.p.m. The doctor rests on two ball bearings and is loaded with adjustable weights. A shallow colour box which can be easily raised and lowered allows the roller to revolve in the printing colour direct (Fig. 2) without the intervention of a feeding roller, which would make measurement difficult. Finally, the measuring device consisted of a sensitive ammeter, on which any variation in friction was recorded as a visible rise or fall in the current.

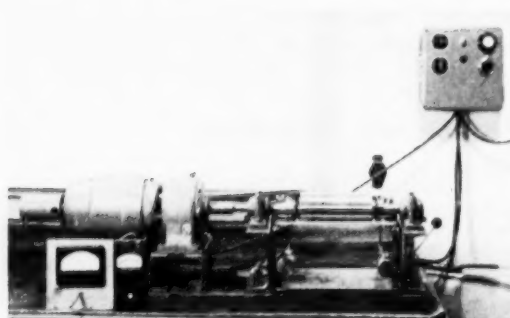


FIG. 1

This simple device gave very satisfactory results, although it possessed certain shortcomings. Nevertheless, it proved the correctness of the above theory.

RESULTS

Fig. 3 gives the results of the first experiment designed to show the dependence of friction on the concentration of the thickener at printing speeds varying from 20 to 120 r.p.m. From relatively high values on the right-hand side, due to tackiness of the print paste—gum arabic (1 : 1)—the curves

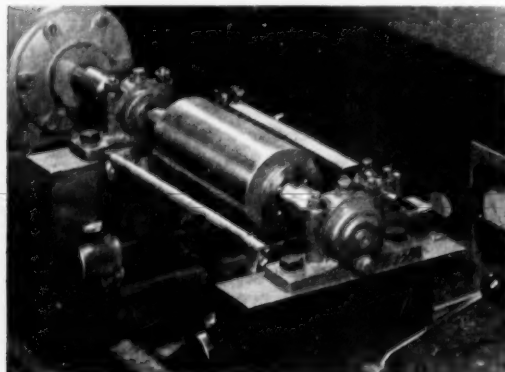


FIG. 2

drop rapidly to a minimum, which corresponds approximately to the normal concentration (60%) of this thickener in printing colours, and rise again, fairly steeply, towards the value for pure water. Thus 60% gum arabic (1 : 1) exhibits a definite lubricating effect, whereas water is a very poor lubricant. Indeed, when the copper roller was run for 10 min. in water at a speed of 120 r.p.m. with full weight on the doctor, the roller was badly damaged, and had to be polished before a new trial could be started. All subsequent trials showed that above a friction value of 200 arbitrary units there begins the "zone of roller damage".

Table I gives the maximum and minimum friction values for various thickenings at different concentrations. Except in the case of gum arabic, which is a tacky mass in its concentrated form and

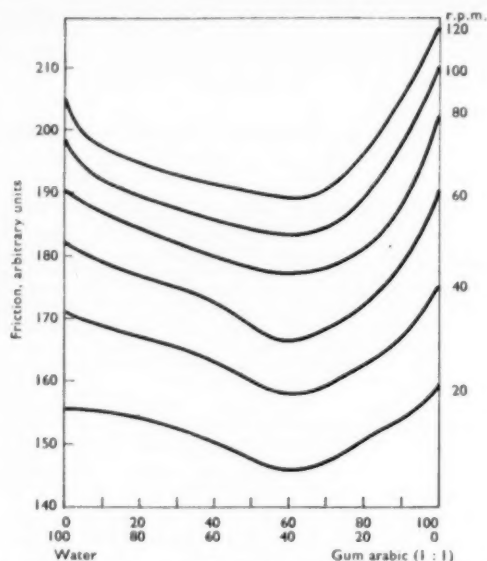


FIG. 3—Effect of Concentration of Neutral (pH=7) Gum Arabic Thickening on Friction Values at Various Roller Speeds

gives more adhesion to the doctor blade, all values over 200 indicate poor lubrication. In this respect crude carboxymethyl cellulose is a real "abrasive". According to the minimum values listed in Table I, gum arabic, crystal gum, starch-tragacanth, British gum, tragacanth, and Solvitose C exhibit the best working properties in normal printing

TABLE I
Friction Values (Maximum and Minimum)
and Viscosities of Various Thickenings

(Roller speed = 120 r.p.m. pH = 7) (Friction value for pure water = 205)			
Thickening	Concn. (% by wt.)	Friction Values*	Viscosity (centipoises)
Gum arabic (1 : 1)	60	189	234
	100	216	5900
Crystal gum (1 : 2)	60	187	1250
	100	194	16000
Starch-tragacanth	80	180	4500
	100	196	11800
British gum (1 : 1)	70	172	142
	100	186	2600
Tragacanth (6%)	60	189	910
	100	208	4300
Locust-bean gum (2%)	65	195	1280
	80	211	2420
Sodium alginate (6%)	60	191	244
	100	192	3400
Carboxymethyl cellulose (crude, 8%)	60	260	476
	100	226	2900
Carboxymethyl cellulose (salt-free, 4%)	80	200	2300
	100	195	5700
Solvitose C (Scholten) (10%)	50	200	134
	100	187	750
Solvitose H (Scholten) (25%)	60	200	—
	100	196	—
Solvitex ST (Scholten) (10%)	60	202	336
	100	206	2600
Potash thickening	80	183	1400
	100	196	9600

* Arbitrary units.

viscosities, a statement which is fully confirmed by practical experience.

In Table I, besides the friction values, the viscosities for every tested sample have been recorded to show that there is not the slightest correlation between these two characteristics.

Table I shows also the poor lubricating properties of many thickenings of low dry content.

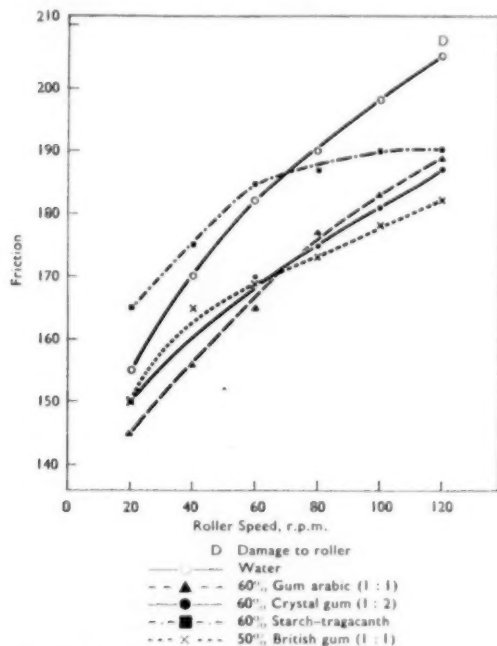


FIG. 4—Thickenings of High Dry Content (pH = 7)

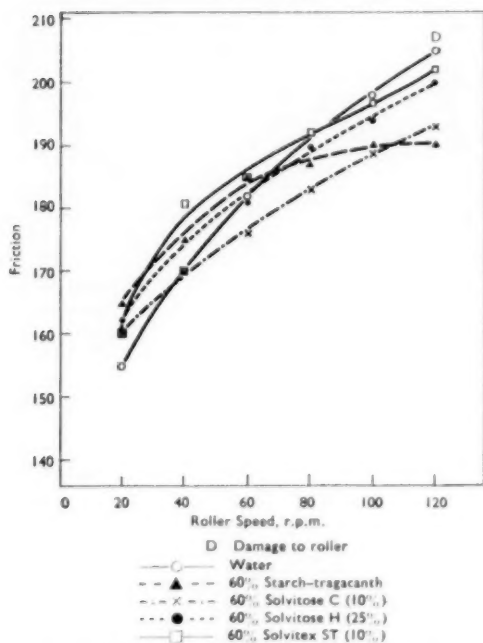


FIG. 5—Thickenings of Medium Dry Content (pH = 7)

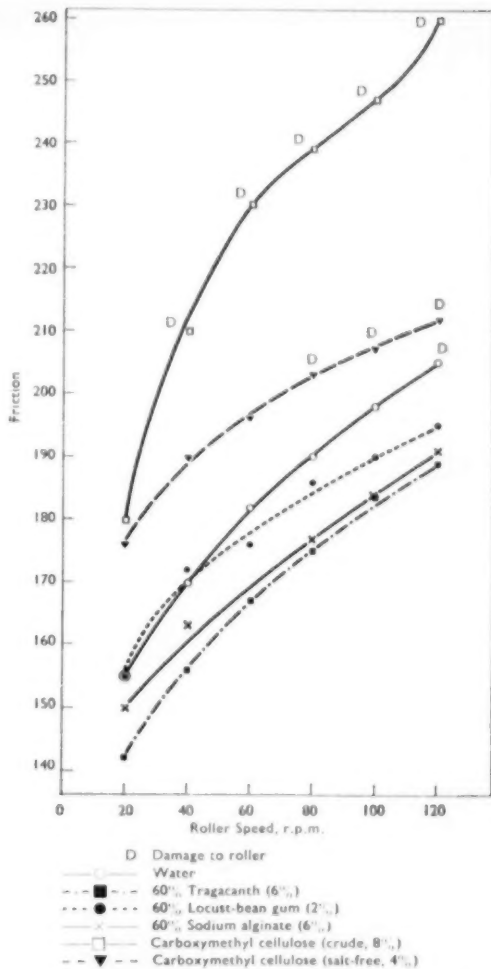


FIG. 6—Thickenings of Low Dry Content (pH = 7)

In Fig. 4-6 three groups of curves are assembled showing the behaviour, compared with water, of thickenings of high, medium, and low dry content respectively, the friction values being plotted against printing speed. It will be observed that the curves for thickenings of high dry content (Fig. 4) lie well below that for water, whereas those for thickenings of medium dry content (Fig. 5) approach it closely. Starch-tragacanth differs from other thickenings in that its friction value does not rise proportionally to increasing printing speed. Thickenings of low dry content are characterised by steeply ascending curves (Fig. 6), which at high printing speeds will probably reach the "damage zone". Carboxymethyl cellulose actually lies above the curve for water and is, for roller printing purposes, a thickener of poor working properties.

The performance of carboxymethyl cellulose can be much improved if a lubricant is added (Fig. 7), olive oil being the most effective in the present case. It makes no difference whether the oil is added as such or as an emulsion. The dotted curve in Fig. 7

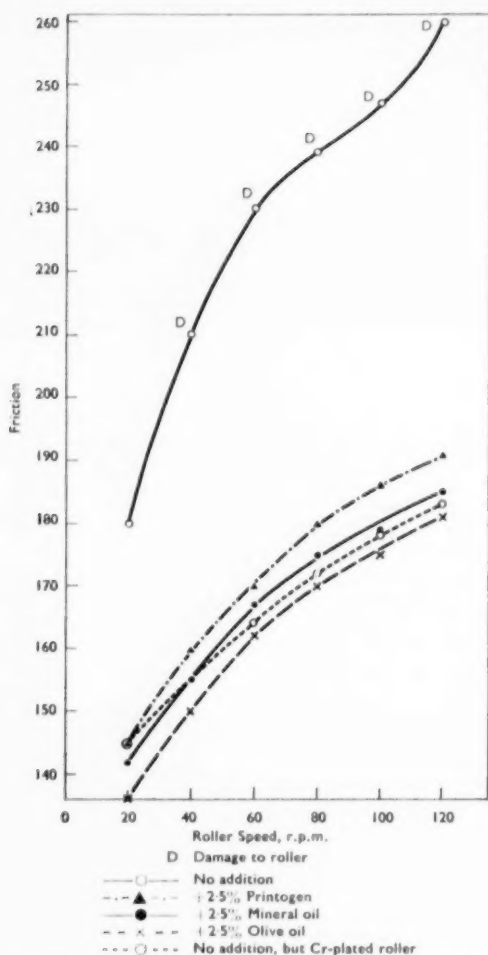


FIG. 7—Effects of Lubricants and of Chromium-plated Roller on Performance of Crude Carboxymethyl Cellulose (8%) (pH = 7)

represents the same thickening without any addition in contact with a chromium-plated roller. What we were tempted to call an "abrasive" for copper rollers thus behaves quite normally when copper is replaced by chromium.

Up to this stage strictly neutral thickenings had been examined. But, as the printer has to deal almost as frequently with alkaline or acid colours, it was necessary to investigate the influence of variations in pH. The results of this investigation were surprising, inasmuch as the different thickenings showed an individual behaviour. For instance, in the case of starch-tragacanth to which acetic acid had been added, the friction curve rose very high and caused considerable damage to the roller, whereas addition of alkali caused only slight change in or even—as in the case of potash—improved lubrication compared with the neutral thickening. On the other hand, with tragacanth (Fig. 9) on the acid side friction was lower—especially at lower printing speeds—while on the alkaline side higher friction and incipient roller damage were noted.

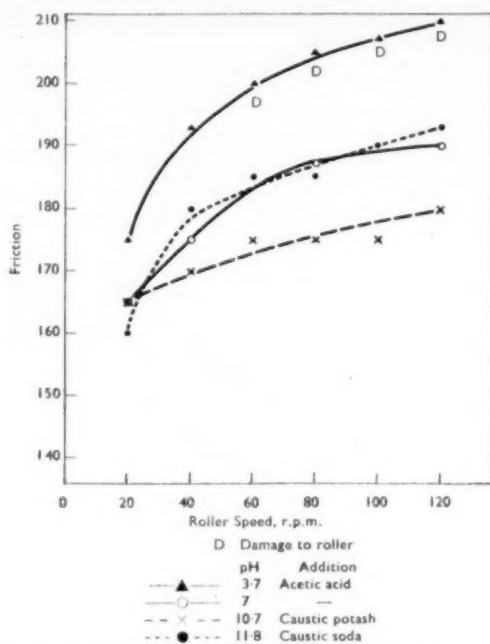


FIG. 8—Effect of pH on 60% Starch-Tragacanth

A further experiment showed that results obtained with thickenings alone, even when various pH conditions are considered, cannot serve to predict the performance of printing pastes containing an increased number of ingredients, as e.g. vat printing pastes. Thus Fig. 10 reveals a complexity which still requires a satisfactory explanation:

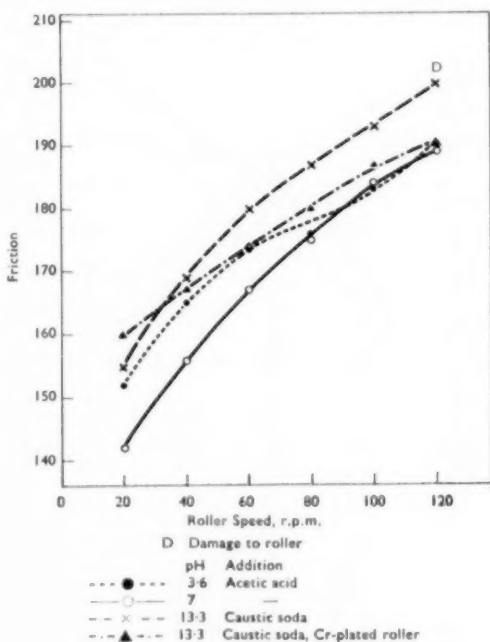


FIG. 9—Effect of pH on 60% Tragacanth (6%)

starch-tragacanth with potash added gave lower friction values than a potash thickening containing starch-tragacanth, British gum, glycerol, and potash, but a printing paste prepared with the potash thickening showed more promise of smooth running than the colour thickened with plain starch-tragacanth.

Finally, it was of considerable interest to investigate the running properties of some modern thickenings of the emulsion type used in pigment

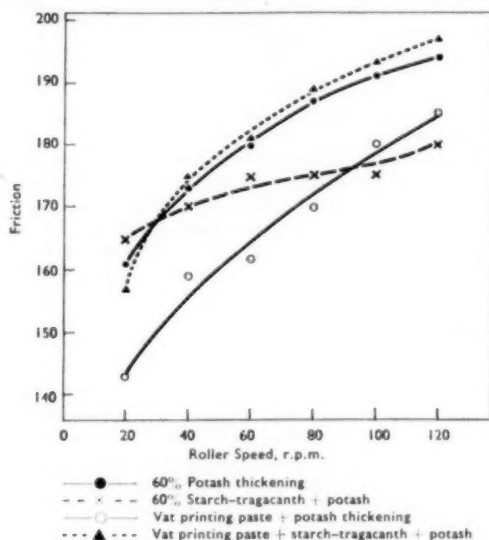


FIG. 10—Effect of Complexity of Printing Paste

printing. Five different pigment printing pastes of the oil-in-water type and one of the water-in-oil type, all containing the same pigment, viz. Phthalocyanine Green, were investigated. As expected, the measurements showed that the water-in-oil type, with its continuous oil phase and distinct lubricating properties, has a marked advantage (Fig. 11).

CONCLUSIONS

Summing up, it may safely be stated that this new approach to a detailed investigation of the undetermined "working properties" of thickenings and printing pastes shows some promise. The method will obviously have to be complemented by rheological studies, which are not the author's special field. The results obtained are only qualitative, and information on new examples can be derived only by comparison.

The measuring device described will certainly prove most useful in testing the effectiveness of various printing assistants recommended for

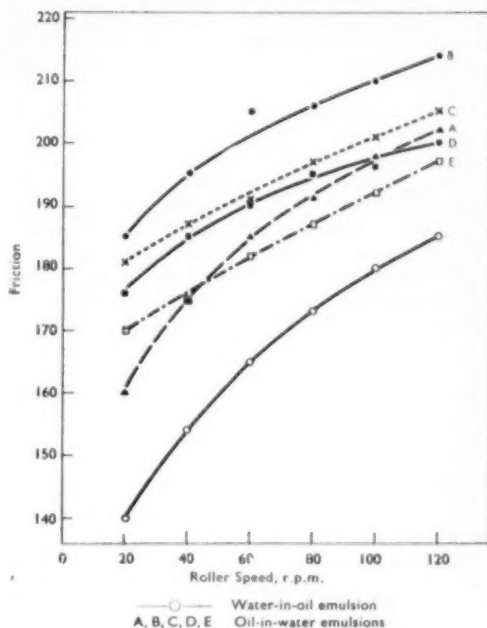


FIG. 11—Emulsion Thickenings

improving the working properties of print pastes under practical conditions and in evaluating their performance numerically.

The method requires several improvements, especially with regard to accuracy of measurements. But, all things considered, the first step, at least, has been taken towards overcoming a frequent difficulty, which in some printworks has developed to a positive plague. The majority of printers have found that the most effective means of avoiding this difficulty is to replace copper rollers by chromium-plated ones. This measure serves to reduce friction values to normal, and gives support to the author's theory.

I am indebted to Messrs. Ciba Ltd. for having given me the opportunity of carrying out this investigation. I should also like to extend my thanks to Messrs. M. Jankowski, who constructed the measuring apparatus, R. Winkler, who supervised the experimental work, and N. Bigler, who contributed photographs and slides.

CIBA LTD.
BASLE
SWITZERLAND

(MS. received 3rd July 1953)

Reference

¹ Krähenbühl, E., *Melliand Textilber.*, **22**, 484 (1941).

Discussion

Prof. J. B. SPEAKMAN: Has any work been carried out on the behaviour of copper rollers to which Fluon (poly-tetrafluoroethylene) has been applied? The lubricating efficiency of the Fluon is so great that doctor streaks of the type described by Dr. Krähenbühl should be eliminated, but I

do not know whether other factors would preclude the use of Fluon.

Dr. E. A. KRÄHENBÜHL: I am not familiar with this treatment of metals. But it can be expected that, if the presence of Fluon does not in any way affect the properties of printing colours and a

substantial reduction of mechanical friction between doctor and roller is achieved by this treatment, it may be effective in preventing doctor streaks.

Mr. F. CROMPTON: When printing citrate of soda using starch thickening even with added oil the printing paste after running a short time, suddenly forms hard crystals that score the copper roller deeply. This does not happen with British Gum thickening. Is this crystal formation due to electrolytic action? Would Fluon-coated rollers lead to deep scoring of the copper rollers?

Dr. KRÄHENBÜHL: Salts like citrate of soda show a marked tendency to form supersaturated solutions (a good example is also copper citrate). I suppose that in starch tragacanth thickening the tendency to crystallize is less impeded than in British gum with its higher dry content. Any formation of crystals in a printing paste creates conditions which, apart from frictional properties, must lead to roller damage. Use of Fluon-coated rollers would only give an improvement if a harder surface is produced by this coating.

Dr. T. VICKERSTAFF: In experiments of this kind, it would seem essential to use a roller with a reproducible and constant surface. Presumably however, it is necessary to repolish the roller at intervals and this may lead to a gradual surface hardening of the roller. How was this controlled?

Dr. KRÄHENBÜHL: The roller used was not a new one and had been re-polished many times before and during these experiments. So a fairly constant condition of its surface could be assumed, although it has not been specially controlled.

Dr. VICKERSTAFF: The friction value of 200 seems to be a critical value beyond which roller damage is always observed. The only exceptions are in the case of the oil-in-water thickenings BeC in Fig. 11. Is any reason known why such emulsions produce no damage at the high friction level?

Dr. KRÄHENBÜHL: The absence of roller damage with certain oil-in-water emulsion colours even at printing speeds which exceeded a friction value of 200—critical in all other cases—is indeed surprising and not fully understood. Possibly the presence of an oily liquid, even if in the inner phase is responsible for this result. In our experiments a trial was never extended over 15 minutes and it is not excluded that roller damage would have occurred afterwards.

Mr. R. THORNTON: In view of the characteristic curves which have been produced as a result of this investigation, would the lecturer suggest that certain thickenings would give a greater freedom from doctor damage, as distinct from roller damage, on the assumption that the printing paste does contain some undesirable foreign matter in the form of grit, etc.?

Dr. KRÄHENBÜHL: No. This investigation is mainly concerned with roller damage, which generally precedes doctor damage if the primary cause is excessive friction. The presence of foreign matter in the form of hard particles contained in the printing paste will cause roller and doctor damage

with any thickening, regardless of its frictional characteristics.

Mr. J. W. RUWHOF: I would like to know whether Dr. Krähenbühl intends to go on with his most valuable research. Some points of interest are e.g.—

(a) in Fig. 7 of his paper there is one curve of a chromium-plated roller. Is there more evidence—or will there be—that chromium-plated rollers completely eliminate this cause of doctor streaks?

(b) the influence of the angle of contact between doctor blade and printing roller.

(c) the influence of the engraving of the printing roller.

Dr. KRÄHENBÜHL: Yes. We shall pursue this investigation.

(a) In our trials roller damage was never noted when chromium-plated rollers were used. But this obviously does not mean that this would be impossible if very severe conditions were chosen.

(b) Certainly there is an influence of the angle of contact between printing roller and doctor blade. The smaller the angle the less danger of damage. Hard particles would then more easily get an opportunity to slip away under the edge of the blade without damaging the roller.

(c) So far we have not used engraved rollers. An influence of the engraving is at least probable. As far as mill-engraving is concerned, a hardening action of the mechanical pressure between the "mill" and the raw roller must reduce the tendency of the latter to become scratched.

Mr. RUWHOF: In Fig. 4 of the preprint the starch-tragacanth curve is of particular interest. In his lecture this morning Dr. Krähenbühl said that Derry and Higginbotham threw new light on this. Yet Dr. Krähenbühl gives in Table I figures which prove there does not exist agreement between friction values and viscosities. This is not quite clear, because in my opinion there is evidence of relation between these two, if only the viscosity at a higher shearing stress is taken.

Dr. KRÄHENBÜHL: The relations between friction values and viscosities are not of a simple mathematical nature. The unusual behaviour of starch-tragacanth thickening, which, at higher printing speeds, according to the diagram in Fig. 4 and 5, shows no rise in friction values, is due in my opinion to a homogenising action of its being laminated between roller and doctor, a phenomenon therefore which is comparable to Mr. Derry and Mr. Higginbotham's findings at higher shearing stresses. But homogenisation does not necessarily mean loss of viscosity.

Mr. RUWHOF: I would like to know whether Dr. Krähenbühl thinks damage caused by electrochemical corrosion of negligible importance, or intentionally left this subject aside?

Dr. KRÄHENBÜHL: Certainly electrochemical corrosion is another possibility of roller damage. Earlier work by Reinking suggested it to be the main cause of it. In my experiments it was deliberately left aside and, as far as possible, eliminated.

Mr. N. W. YELLAND: To what extent was the sharpness of the doctor edge controlled in these experiments? Sharpness of edge is important in every way, and declines rapidly during running due to wear which produces a continually increasing arc of contact. This may not make much difference to the total frictional force, which is what is in effect registered by the ammeter, but it would affect the intensity of pressure per unit area of the arc of contact, and might thus have an influence on the shearing of the thickening through the contact zone.

Dr. KRÄHENBÜHL: I agree with Mr. Yelland. The sharpness of the doctor's edge will gradually decrease the longer the roller is kept running. Our measurements were always made in the initial stages of every trial, i.e. as soon as a constant value was recorded by the ammeter; later modifications have not been registered. A survey of the behaviour of thickenings in relation to time would have to take into account Mr. Yelland's considerations.

Mr. H. B. HAMPSON: Roller damage. It has been observed over a number of years that "ploughing up" of copper rollers (distinct from attack on doctor blade) is associated with certain conditions.

1. In the majority of cases it has occurred on old rather than new printing machines.

2. It has tended to confine itself to rollers late in the sequence of the pattern.

3. It is confined to alkaline print pastes, notably caustic vat colours, and with vat colours is particularly associated with Blue GCP and Caledon Jade Green.

4. It does not seem to occur when stainless doctors are used, or when rollers are chromium-plated.

Whilst these facts confirm Dr. Krähenbühl's observations to some extent, does he think that there is evidence here in support or at any rate partly in support of the theory that this fault may be primarily electrical in origin?

Dr. KRÄHENBÜHL: I would never go so far as to pretend that friction as described in my paper is the only cause of roller damage. But it is one that has always been overlooked and is liable to furnish an explanation for many cases where all other considerations fail. In my own experience as a print-works colourist I found roller damage often associated with certain dyes amongst which Blue GCP was one. This trouble was mostly linked with a pronounced tendency of these colours to scum. This would suggest the occurrence of a breakdown of the otherwise continuous film of colour between doctor and roller and possibly provoke a higher degree of friction.

The use of stainless doctor blades instead of steel blades reduces friction as in the case of brass or bronze doctors which I tried, and the use of chromium-plated rollers is one more step in this direction.

Mr. R. K. FOURNESS*: It is assumed that the unsatisfactory nature of the crude carboxymethyl cellulose paste used is due to the presence of dissolved salt. Has the effect of addition of salt or

other electrolytes to other thickeners been examined? Would the lecturer expect the properties of a printing paste to be adversely affected by the inadvertent introduction of salt which may be present e.g. in the colour paste as supplied by the dye maker?

Dr. KRÄHENBÜHL: I see that my investigation is rather incomplete. My only excuse is that all experiments had to be done within 7 weeks. So this feature has not been examined. We studied the influence of pH by making additions of acetic acid and different compounds of alkaline nature to thickenings. The study of salt—or more generally electrolytes—has not yet been investigated. Presumably inadvertent introduction of salt, as Mr. Fourness assumes, would not visibly affect the behaviour of thickenings or print pastes. In the case of crude carboxymethylcellulose the salt content amounts to nearly 50% of the dry product.

Mr. N. HAMER*: It would add materially to Dr. Krähenbühl's valuable contribution if the investigation could be extended to conform more closely to works conditions. Substitution of a longer, engraved roller for the short, polished one, already used, and a traversing doctor in place of the fixed one might have a marked effect in frictional resistance.

The behaviour of pigment printing pastes is interesting and will bear further investigation. In these oil in water and water in oil emulsions the hydrophobic constituent is frequently a substance with very little lubricating value, and in Fig. 11 the frictional resistance of pastes A to E is high, eight values of 200 or over being recorded, yet no damage was sustained, whereas in all the other pastes examined 200 was very critical.

Dr. KRÄHENBÜHL: In order to adjust an experimental set-up to conform more closely to works conditions, quite a series of modifications would be necessary. But I ask myself whether they would not introduce so many more variables into the picture. I rather see the necessity to make the measuring device more accurate and sensitive, e.g. by introducing a spring to take up the load between the driving motor and the driven axle. As regards lubricating properties of hydrophobic constituents in water-in-oil emulsions, I would not normally consider them as lubricants *in sensu stricto* but, in comparison with water, they evidently secure an easier gliding of the doctor on the roller surface.

Mr. W. PENN*: It may be possible to prevent doctor streaks, i.e. streaks caused by a damaged doctor blade, by rendering the tip of the blade more resistant to damage. Can the lecturer state whether this has been tried?

Dr. KRÄHENBÜHL: This is the point where we have to differentiate between doctor streaks and roller damage. A harder edge of the doctor blade will prevent hard particles from cutting through the tip of the blade and rather lead to roller damage. If the solid matter does not remain under the doctor but rather escapes by lifting it or damaging it, the roller will not suffer but a series of occasional, repeated or continuous printing faults will result. — Trials in the direction suggested were not made.

Mr. H. A. TURNER*: This simple but very ingenious transformation of the roller-doctor system into a friction-meter is extremely interesting. Does it not give other information too? For example, in Fig. 3, where the energy necessary to maintain rotation is plotted against concentration, it may be that, as Dr. Krähenbühl suggests, there is a direct measure of the lubricant effect of the paste while the concentration of thickener remains low. But why does the energy consumption pass through a minimum as the gum concentration is increased? Is the relatively high energy consumption at higher concentrations due to a viscosity effect, the more viscous paste being carried up on the roller in larger amounts and being churned round behind the doctor exerting a viscous drag on the roller? If this were so, the instrument would need to be considered as a friction meter at one end of its range and a viscometer at the other.

Could it not also be modified, with a lightly-weighted doctor capable of movement along the periphery of the rotating roller, to measure the adhesion of paste to copper, a quantity that would be of great interest?

Dr. KRÄHENBÜHL*: Energy consumption in the roller-doctor system as used to determine friction conditions, is naturally not related to friction alone, or—more exactly—only for low concentrations of the thickener, from pure water as an intermediate film between roller and doctor to about normal concentrations of thickeners in print pastes which, owing to a lubricating action of the thickener show lower friction values than water. The right side of Fig. 3 with ascending curves shows very distinctly the viscosity effect exactly as Mr. Turner describes it. My measurements published in all the following diagrams were made under conditions where viscosity as a drag on the roller becomes negligible. Distinctly measurable differences, however, showed up in the ammeter when the roller, without a doctor on its surface, revolved in water or in a viscous thickening.

Mr. E. KERSHAW*: I would like to enquire from Dr. Krähenbühl—

1. What type of viscometer was used in his experiments?

2. What was the angle of contact and the pressure of the doctor blade on the copper roller since it would seem that even more informative and

comparable results might be obtainable if the pressure applied by the doctor was varied according to the apparent viscosity of the printing pastes.

Dr. KRÄHENBÜHL*: 1. The viscometer employed was a "Drage"-Viscometer supplied by Dr. A. G. Epprecht, Zürich, which can be used to measure the viscosity of Newtonian and structurally viscous mediums ranging from 0.5 to 1,000,000 cP. A series of different stirrers is used at three different speeds of the driving motor (20, 64 and 200 r.p.m.).

2. Angle of contact and pressure of the doctor blade have an influence on the friction values measured. Higher pressure results in higher values. In our trials pressure was kept constant by adjusting the weight on the levers in a position where the variations between different thickenings or printing speeds were greatest. The angle of contact within the range normally used was not critical and could be neglected.

Mr. K. A. HILTON*: Referring to Table I, I note that sodium alginate (6%) has friction values of 191 and 192 respectively. Dr. Krähenbühl states in his paper that according to the minimum values listed in Table I, gum arabic, crystal gum, starch-tragacanth and Solvitose C exhibit the best working properties in normal printing viscosities. Since the friction value for sodium alginate is below 200, I wondered why the author did not include this thickener in those mentioned as having the best working properties and if he cares to comment upon this point.

Dr. KRÄHENBÜHL*: I did not want to disqualify sodium alginate as a thickening agent, which amongst those with low dry content, owing to its very homogeneous nature, is one of the very best for textile printing. If I did not mention it together with gum arabic, crystal gum, British gum and starch-tragacanth it was solely because I had in mind thickenings with high to medium dry content.

Mr. N. B. KATRAK*: Is it possible to use doctor blades made of brass instead of steel, to prevent doctor streaks?

Is it an established method in print works?

Dr. KRÄHENBÜHL*: Brass blades could be used with success, but, as they are subject to a more rapid wear and need to be re-sharpened more often, printers do not like them. They frequently use them as lint doctors where the blade is directed against the movement of the roller.

* Communicated

The Flow Properties of Textile Printing Pastes

R. L. DERRY and R. S. HIGGINBOTHAM

The colour pastes employed in the machine printing of textiles are rheologically complex fluids, the viscosity coefficient falling with increase in rate of shear or shearing stress. In order to relate the viscosity of a paste with the quality of the resulting print, it is essential that the measurements of apparent viscosity should be made at the operative shearing stresses. Sharpness of definition is shown to be controlled by the viscosity of the printing paste at a shearing stress of 4500 dynes/sq.cm., and levelness by the viscosity at low stresses of the order of 100 dynes/sq.cm. Viscosity ranges suitable for the printing of fine lines, pegs, and blotches are indicated. The amount of anomaly which can be tolerated in pastes intended for the printing of fine lines is greater than in those intended for the printing of pegs and blotches, where the conflicting requirements of levelness and definition have to be satisfied.

INTRODUCTION

The printing of textiles by the use of engraved rollers has been carried out for about 160 years, and in the course of time many different styles of printing have been developed. The natural dye-stuffs have been largely replaced by the synthetic dyes, but little attention has been directed towards gaining a better understanding of the functions of the thickener, which, in one form or another, is a constituent of every print paste. The reasons for this neglect are not far to seek. The starches, gums, and mucilages used for the purpose are complex substances, both physically and chemically, and those which are natural products vary with the conditions of growth of the parent plant. Furthermore, they frequently undergo chemical modification in the process of manufacture, and are subjected to further chemical and physical change when incorporated into the actual printing paste.

Although, as implied by the very name *thickener*, the rheological properties of pastes are of the greatest importance, generally speaking no single measurement of viscosity will serve to characterise a paste or to predict its behaviour in machine printing. In the present paper an attempt will be made to relate flow behaviour to print quality. It is, of course, appreciated that other factors besides viscosity may determine whether a thickener is acceptable to the printer for a particular purpose.

COEFFICIENT OF VISCOSITY

Newton attributed viscosity to internal friction in the fluid, and defined it in terms of the tangential stress S and velocity gradient dv/dx in a simple shear—

$$S = \eta \frac{dv}{dx}$$

By definition, a fluid has a dynamic viscosity η of one poise when a force of one dyne is required to maintain a difference in velocity of 1 cm./sec. between two parallel planes 1 cm. apart and each 1 sq.cm. in area. More simply, dynamic viscosity is the ratio of shearing stress to rate of shear or velocity gradient. If, at a constant temperature, this ratio is a constant independent of the rate of shear, the viscosity coefficient completely defines the flow properties of the fluid under conditions of laminar flow. Lubricating oils, sugar solutions, and vegetable oils are fluids of this type, which are consequently termed *Newtonian fluids*, but there are many fluids of great industrial importance which do

not obey this simple law, e.g. paints, printing inks, food products, and most types of textile printing pastes. The anomalous flow behaviour of printing thickeners is generally shown by a fall in the viscosity coefficient with increase in the rate of shear ("shear-rate thinning"). When the coefficient varies in this way with rate of shear, it is often called an *apparent viscosity* η_a . If the pastes are thixotropic, the viscosity does not immediately return to its original value when the rate of shear is reduced again. The simplest way of describing complex flow behaviour is by means of curves in which shearing stress is plotted against rate of shear, or apparent viscosity against either of these functions. Because of the magnitude of the changes it may be necessary to use doubly logarithmic plots. To provide the information for such flow curves it is necessary to employ an instrument which will enable measurements of apparent viscosity to be made at definite rates of shear or shearing stress over the range covered in the process to be controlled. The cone-and-plate viscometer¹, especially when equipped with infinitely variable speed control, as in the commercial Ferranti-Shirley instrument, covers a sufficiently wide range for the detailed examination of printing pastes.

BEARING OF RHEOLOGY ON ROLLER PRINTING

During its progress through the machine a printing paste is subjected to a wide range of shearing stresses. In the colour box it is sheared between the stationary walls and the rotating furnishing roller, and although the rate of shear here may not exceed 50 sec.⁻¹, the apparent viscosity of highly anomalous pastes may be reduced considerably. Shearing forces of uncertain magnitude will be called into play between the furnishing and the engraved rollers, but these will be small compared with those operating under the cleaning action of the doctor. Since the film on the unengraved parts of the roller is extremely thin and the maximum depth of the engraving possibly not more than 0.01 in., the paste retained by the roller, and to a lesser extent that returned to the colour box, will have been subjected to very large stresses, which may cause an irreversible loss of viscosity of pastes which are unstable to shear.

The operations of furnishing and cleaning only indirectly affect print quality. They are of smaller moment in the present context than the factors concerned in the transfer of colour from the engraving to the cloth, which have important

bearings on definition, levelness, and penetration. During transfer of the paste it is subjected to a high, almost instantaneous, shearing stress, shown later to be about 4500 dynes/sq.cm., and under the influence of this stress the paste flows through the interstices of the cloth and may in certain circumstances go on to the blanket or back grey.

Apart from flushing, which is liable to occur when the volume of the engraving is large in relation to the absorbency of the cloth, the paste tends to spread beyond the boundaries of the design, and this is resisted by its viscosity at the above stress. After this stress is released, the colour will redistribute itself within the pattern if sufficiently fluid at low shearing stresses of the order of 10–100 dynes/sq.cm.

The shearing stress operating during printing cannot be calculated on account of the many factors involved. It has, however, been determined experimentally from the results of many printing trials; the method adopted makes use of the different degrees of anomaly exhibited by printing thickeners.

There are three main groups of thickeners. One comprises materials such as the unmodified starches and natural gums, e.g. tragacanth and karaya and locust-bean flour, all of which give highly viscous pastes at low concentrations. This type is further characterised by a high degree of anomaly, the apparent viscosity of the pastes containing them falling rapidly with increase in shearing stress or rate of shear. This type of behaviour is usually associated with the presence of swollen particles, highly flexible long-chain molecules, or aggregates which are elastically deformable and change their shape progressively with rising stress in such a way as to make flow easier.

Comprising the second group are thickeners such as gum arabic and the highly modified British gums, which yield very viscous pastes at high concentrations. Their flow curves are nearly Newtonian and show only a small degree of anomaly.

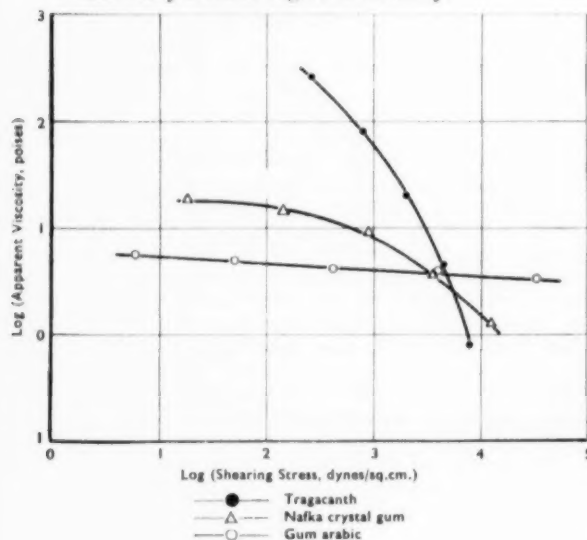


FIG. 1

Intermediate in character are the British gums containing varying proportions of slightly modified or unmodified starch, modified karaya gum, products such as Nafka crystal gum (a modified natural gum), and, of course, mixtures containing compatible members of the two main groups. They yield pastes which are frequently Newtonian in character at stresses up to 100 dynes/sq.cm. and anomalous at higher stresses.

Flow curves representative of colour pastes containing thickeners from each group are given in Fig. 1, but it should be realised that the flow properties of highly anomalous thickenings are very dependent upon the conditions of preparation. This may be illustrated by reference to the changes occurring during the preparation of a paste containing 5.5% of "medium flake" tragacanth which was heated and stirred at 95°C. for periods of up to 48 hr. These are depicted in Fig. 2. After

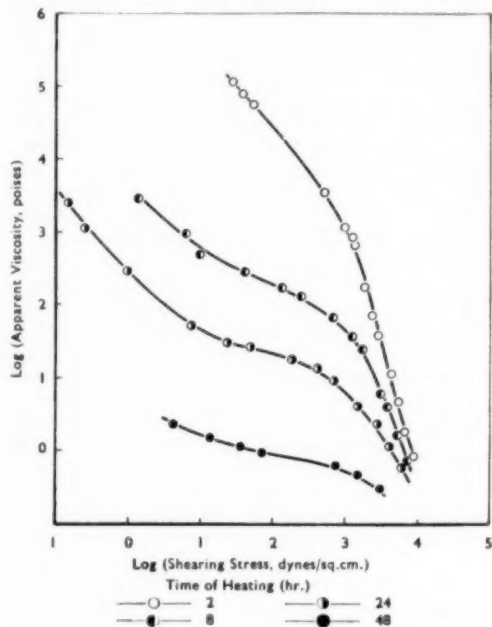


FIG. 2

2 hr. the paste is highly anomalous and extremely viscous at low stress. Both the anomaly and the apparent viscosity decrease progressively with the duration of heating, until after 48 hr. the paste is almost Newtonian but has become so fluid as to have little value as a thickener. These changes in flow properties are associated with the dissolution of the initially insoluble bassorin, which forms one fraction of the gum, and with the chemical degradation of the soluble tragacanthin fraction. Under slightly acidic or alkaline conditions these changes are greatly accelerated, and where viscosity control is exercised they may prove useful in reducing the time of boiling of an insoluble gum.

Dilution of a stock solution of thickener, while reducing the viscosity, does not, unless considerable, cause any great change in the character of the flow

curve. Use was made of the large differences in the flow behaviour of thickeners to determine the operative shearing stress in printing.

EXPERIMENTAL DETERMINATION OF THE OPERATIVE SHEARING STRESS IN ROLLER PRINTING

Vat-dye pastes were prepared containing potassium carbonate (10%), Formosul (Br) (8%), and Caledon Printing Jade Green XNS (ICI) (10%) with different amounts of one of the following thickeners—gum arabic (nearly Newtonian), a modified natural gum (Nafka crystal gum—moderately anomalous), and tragacanth (highly anomalous). The conditions of preparation of the printing pastes were as follows—

GUM ARABIC—The gum was wetted with the diluted dye dispersion and allowed to stand overnight. The paste was then heated, gently stirred to avoid entrapping air, and cooled before addition of potassium carbonate and Formosul. Printing pastes containing from 34.4 to 16.0% of gum were prepared by dilution, further additions of dye, alkali, and reducing agent being made in order to maintain constant concentrations of these components.

NAKFA CRYSTAL GUM (Scholten, Holland)—No special precautions were needed with this material, which is readily soluble in cold water. Pastes containing from 20.4 to 7.5% by weight were prepared.

TRAGACANTH—A stock solution containing 7% by weight of "medium flake" tragacanth was prepared by soaking the gum in water for 3 days. The paste was then heated for 3 hr. at 99°C. in a sulphonation pot fitted with a gate stirrer, and was stirred while cooling. Additions of potassium carbonate, Formosul, and dye were made to the diluted paste shortly before printing. In this way the changes in viscosity arising from the alkali lability of the gum were minimised. The completed pastes contained 5–2% of thickener.

Flow curves were constructed for each paste from viscosity measurements made with a Couette-type rotational viscometer (1.7–66 sec.⁻¹) and a Shirley consistometer² fitted with a cone-and-plate attachment (278–7530 sec.⁻¹)*. Prints were made on a thoroughly scoured and bleached poplinette (110 × 60, 32s × 32s, 3.8 oz./sq.yd.) with a power-operated single-colour machine fitted with a roller engraved with several types and scales of engraving including vertical and horizontal lines. The difference in width between the printed line before steaming and the engraved line is taken as a measure of the spread. Measurements of the spread in several directions were made with a cathetometer. As the spread in the direction of motion of the cloth is always equal to or greater than that in any other direction, that of the horizontal lines was taken as a measure of print definition.

When the amount of spread was plotted against concentration of thickening in the print paste, a series of smooth curves was obtained (Fig. 3). Inspection of the prints suggested that the maximum amounts of spread which can be tolerated in

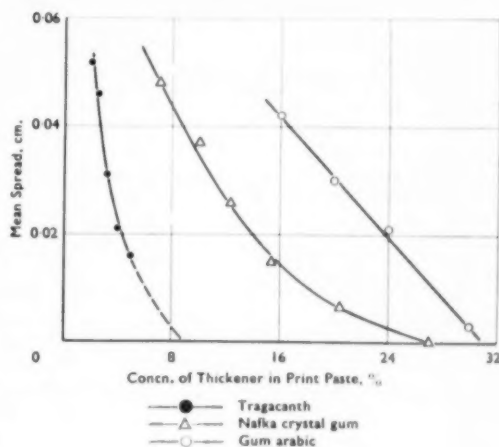


Fig. 3

the printing of fine lines, pegs, and blotches are 0.005, 0.02, and 0.04 cm. respectively. Accordingly, the concentrations of each of the three thickening agents giving these three amounts of spread were then calculated, pastes prepared, and flow curves constructed. Because of differences in anomaly, three different flow curves were obtained relating to a given amount of spread, but they had one point in common, the co-ordinates of which must therefore represent the shearing stress and the apparent viscosity operative during printing. The flow curves in Fig. 1 relate to a spread of 0.02 cm. Mean values of the operative shearing stress and of the apparent viscosity for the three amounts of spread are given in Table I.

Type of Print	Maximum Spread (cm.)	Operative Shearing Stress (dynes/sq.cm.)	Apparent Viscosity (poises)
Fine lines ...	0.005	5350	32.5
Pegs ...	0.020	4000	4.0
Blotches ...	0.040	4300	0.7
Mean	4550	...

If the difficulty of measuring small amounts of spread is borne in mind, the agreement is reasonably good, the largest deviation from the overall mean of 4550 dynes/sq.cm. corresponding to a difference in spread of about 0.004 cm. The results given in Table II relate the maximum spread to the concentration of thickener and the apparent viscosities of the printing pastes at stresses of 100 and 4500 dynes/sq.cm. The anomaly index is expressed as the ratio of the apparent viscosities of the paste at 100 and 4500 dynes/sq.cm. On this scale a Newtonian fluid will have an index of unity, the value for other systems increasing with the degree of anomaly.

A smooth curve relates apparent viscosity at 4500 dynes/sq.cm. to the amount of spread, irrespective of the type of thickener employed (Fig. 4), confirming the validity of the above method for determination of the operative stress. A photographic enlargement (×5) of strips of the poplinette

* These experiments were carried out before the Ferranti-Shirley viscometer became available.

TABLE II
(Width of engraved line = 0.047 cm.)

GUM ARABIC		(width of engraved line = 0.047 cm.)				
Concn. of gum in paste, %...	...	16.0	20.0	24.0	30.0	36.4
Apparent viscosity (poises) at—						
100 dynes/sq.cm. (i)	0.89	1.70	5.50	26.3	83.2
4500 dynes/sq.cm. (ii)	0.79	1.41	4.30	22.4	63.1
Anomaly index (i/ii)	1.12	1.21	1.28	1.17	1.32
Mean vertical spread, cm.	0.0423	0.0302	0.0210	0.0035	-0.001
NAFKA CRYSTAL GUM						
Concn. of gum in paste, %...	...	7.5	10.0	12.4	15.4	20.5
Apparent viscosity (poises) at—						27.0
100 dynes/sq.cm. (i)	1.90	3.71	—	28.2	170
4500 dynes/sq.cm. (ii)	—	0.63	2.24	5.50	30.2
Anomaly index (i/ii)	—	5.88	—	5.13	5.60
Mean vertical spread, cm.	0.048	0.037	0.026	0.015	0.007
						0.000
TRAGACANTH						
Concn. of gum in paste, %...	...	2.0	2.5	3.2	4.0	5.0
Apparent viscosity (poises) at—						
100 dynes/sq.cm. (i)	1.41	—	5.0	~168	~447
4500 dynes/sq.cm. (ii)	0.19	—	0.76	3.7	13.5
Anomaly index (i/ii)	7.4	—	6.6	45.4	33.1
Mean spread, cm.	0.052	0.046	0.031	0.021	0.016

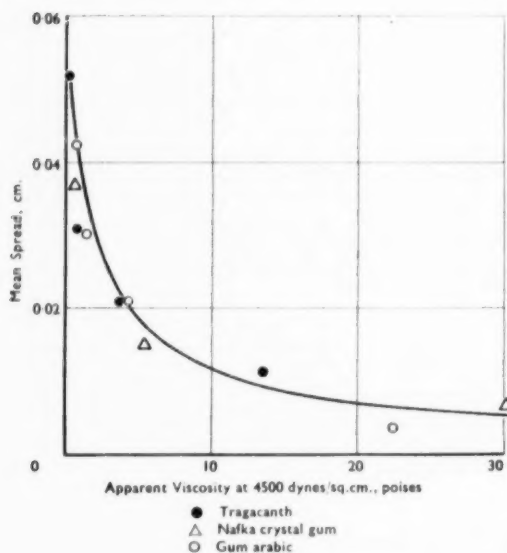


FIG. 4

fabric printed with Caledon Jade Green XN pastes containing gum arabic is reproduced in Fig. 5. This clearly illustrates the relationship between the apparent viscosity of the paste at the operative shearing stress and the quality of definition obtained in the printing of fine lines.

RELATIONSHIP BETWEEN FLOW BEHAVIOUR AND PRINT LEVELNESS

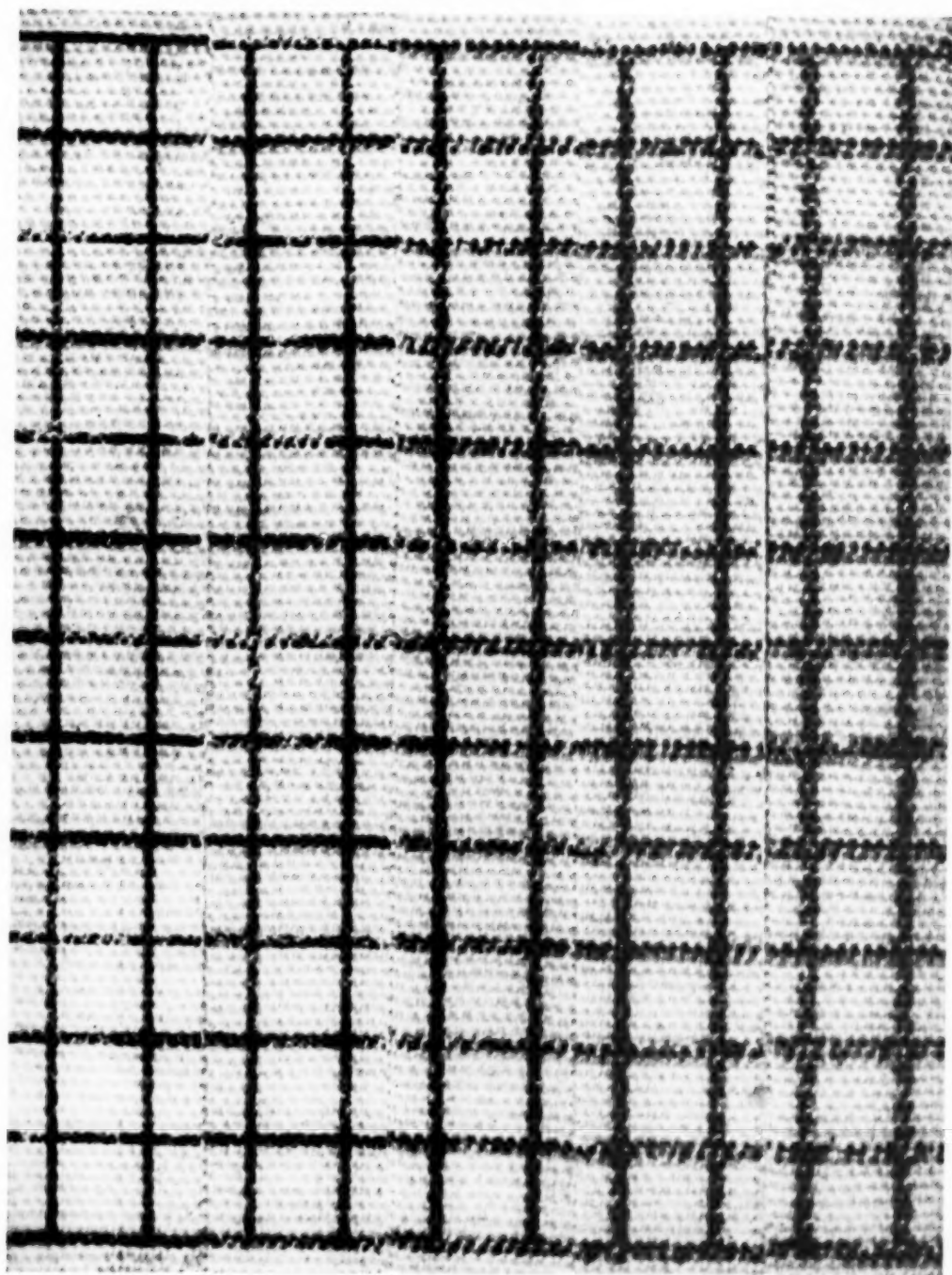
The other bearing of flow behaviour on print quality is concerned with levelness, which is of greater importance in the printing of large patterns, especially blotches, than is definition. Uneven prints can, of course, result from many causes. If the paste is highly viscous at stresses of 10–100 dynes/sq.cm., it tends to lie on the cloth in ridges

corresponding to the lines of the engraving instead of flowing out uniformly over the surface of the fabric. In the absence of any quantitative method of assessing levelness, it is necessary to rely on subjective judgment.

From the examination of a large number of experimental prints on several types of cotton and rayon fabrics covering a wide range of surface textures and cloth structures the general position seems to be clear, although the effect of crushing cannot be examined with a single-colour machine.

The viscosity requirements cannot be stated precisely, for they vary with the character of the cloth. Thus for cloths with a smooth surface such as a cotton poplinette or printer a viscosity of 100 poises at 100 dynes/sq.cm. may not be excessive. On the other hand, for cloths with an uneven surface the upper limit may be less than 30 poises.

This dependence of levelness on low-stress viscosity may be illustrated by results obtained with a number of pastes containing Durindone Printing Blue 4BCS (ICI) (20%), Formosul (8%), potassium carbonate (10%), and a variety of thickening agents. A coarse viscose rayon cloth containing a matt filament warp and a staple fibre weft (84 × 46, 34s × 12s, 4.6 oz./sq.yd.) and presenting an uneven surface was printed with a blotch design, the scale and the depth of the engraving being suitable for this particular fabric. Flow curves were constructed at the time of printing from viscosity measurements made with the Couette-type rotational viscometer and the cone-and-plate instrument. Pastes exhibiting various degrees of anomaly containing gum arabic, highly modified karaya, or mixtures of British gum and maize starch were used, and the prints compared after the usual steaming, oxidising, and soaping treatments. The results (Table III) show that the paste containing gum arabic, which had a viscosity of 12 poises at 100 dynes/sq.cm., gave the most level print, the quality decreasing



63.1

22.4

4.30

1.41

0.79

Apparent Viscosity at 4500 dynes sq. cm. poises

FIG. 5—Photographic Enlargement ($\times 5$) of Cotton Poplinette printed with a Series of Colour Pastes containing 36.4–16.0% of Gum Arabic



TABLE III

Stress, dynes/sq.cm. Thickener	13	50	100	4500	Anomaly Index	Levelness
		Apparent	Viscosity (poises)			
19.0% British gum	6.6	5.0	4.6	2.8	1.6	Poor
1.3% Maize starch						
26.7% Gum arabic	17	13	12	6.8	1.8	Excellent
10.1% Highly modified gum karaya	74	17	13	3.0	4.3	Good
23.4% British gum	105	113	100	10.0	10.0	Moderate
1.6% Maize starch						

with change in low-stress viscosity from this optimum value.

On the other hand, better colour value was obtained on the steamed and washed prints with thickenings containing British gum and maize starch than with gum arabic or modified karaya.

CONCLUSIONS

From a consideration of the requirements of levelness and definition certain conclusions can be drawn.

Firstly, the viscosity of pastes intended for the printing of fine lines must be sufficiently high at a stress of 4500 dynes/sq.cm. to give the required definition. A moderate degree of anomaly may be advantageous, since it assists cleaning, but pastes which are highly anomalous—such as those containing wheat starch or gum tragacanth—may not be sufficiently fluid at low stresses to furnish well unless they undergo a certain amount of breakdown in the printing machine.

Secondly, pastes intended for the printing of pegs and blotches gain little from anomaly. However, thickeners which are nearly Newtonian in flow character have to be used at high concentrations and therefore may give poor colour value. For this reason it may be necessary to reach a compromise between flow behaviour and colour value. A higher degree of anomaly is tolerable in the printing of cotton than of viscose rayon, and therefore some sacrifice of colour value may be inevitable in order to achieve satisfactory levelness on the latter.

Although the various thickeners in common use fall into groups according to the type of flow curve exhibited by the pastes a short time after preparation, it is extremely difficult if not impossible, on account of the many factors involved, to predict what the viscosity levels of any colour paste will be at the operative stresses of 100 and 4500 dynes per sq.cm. Apart from variations in the quality of the products themselves and the influence of the

methods of preparation of the paste, other factors, such as the stability to storage and changes in flow character caused by interaction of the thickener and the dye or other ingredients of the print paste, all complicate the problem of viscosity control.

The behaviour of pastes in machine printing can nevertheless be predicted fairly well from two measurements of apparent viscosity made at low (100 dynes/sq.cm.) and high (4500 dynes/sq.cm.) shearing stresses. Two viscometers have been designed and described² which are suitable for this purpose. One of them—the high-stress instrument—is robust enough for use in a works laboratory.

The form of viscosity control envisaged would be as follows—A print would be prepared with an apparent viscosity at 4500 dynes/sq.cm. appropriate to the degree of sharpness required; if from measurements of low-stress viscosity the paste should be considered satisfactory, it would be subjected to a printing trial. If the paste were too viscous at 100 dynes/sq.cm., the composition of the thickener would have to be modified, for a paste merely containing a smaller proportion of the same thickener would not give a sharp enough print, since its viscosity at 4500 dynes/sq.cm. would then be too low.

* * *

The authors wish to record their indebtedness to Mr. E. Kershaw for much valuable assistance in the preparation of the prints and to Mrs. D. I. Smith for making many of the measurements.

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(MS. received 5th June 1953)

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Discussion

Mr. R. L. HILL: We have observed that oil-in-water emulsion printing thickeners have the property of printing satisfactorily both blotches and fine lines and tend to break down in apparent viscosity when subjected to the high pressures or stresses encountered in homogenisers. This would seem to confirm your observations on the desirable properties of a good working print paste.

Have you conducted any experiments on this type of thickening. If so, what are your conclusions on their properties?

Mr. R. L. DERRY: We have not yet conducted any detailed experiments on emulsion printing

thickeners but these systems are of great rheological interest. Since the particles forming the discontinuous phase are readily deformable under shearing stresses the emulsions are likely to exhibit anomalous viscosity effects but the extent and degree of anomaly could only be determined experimentally.

Dr. W. SHAW: The experiments described in the paper to evaluate the shearing stress operating at the instant of colour transfer from the roller to the fabric have shown the value to be 4500 dynes per sq. cm. Only one type of cloth, a cotton poplinette, has, however, apparently been used for these tests. Would this value be expected to

apply also in the case of very different fabrics such as a high quality cellulose acetate satin or a very coarse absorbent cotton material?

Mr. DERRY: The experiments described in the paper have been repeated using a cotton printer and a heavy cotton sheeting. Both fabrics had been thoroughly prepared for printing. The results confirm the value of 4500 dynes/sq.cm. for the operative stress. Without more information about the mechanism of absorption of paste by the fabric we would not care to suggest that the same stress would operate during the printing of relatively non-absorbent fibres such as cellulose acetate or the newer synthetic rayons. The experimental technique described in the paper would, of course, be applicable to such materials.

Mr. J. W. RUWHOF: Not only the type of the fabric but also the speed of the machine and the pressure between printing roller and pressure roller can influence the spread. Is there anything known about it?

Mr. DERRY: We have deliberately restricted the scope of this paper to the effect of the flow characteristics of the paste upon definition and levelness since these are of major importance. We have not observed any correlation between printing speed and quality of definition over the range 4.2 to 14.3 yards/minute although according to Knecht and Fothergill definition improves with speed up to 130 yds./minute. Since it is possible to obtain a sharp impression at low speeds this must be a second-order effect. Similarly, the load applied to the printing roller is not critical except insofar as slippage in the nip must be prevented otherwise a more precise means of adjusting the load would have been fitted to printing machines during their course of development.

Mr. RUWHOF: What is the influence of the continuous feeding of paste from colour box to printing roller and blading with e.g. thixotropic fluids?

Mr. DERRY: It is true to say that print pastes which are highly thixotropic, that is, those which suffer a large, irreversible fall in consistency when sheared, are not ideal for roller printing as the paste will be broken down in the colour box and the flow curves of such pastes are very much dependent on the conditions of preparation.

Mr. J. A. KIERNAN: Have the authors done any comparative work between homogenised and non-homogenised thickenings and if so what information can they give us, and have they any data on shearing stresses, before and after homogenising?

Dr. R. S. HIGGINBOTHAM: We have examined only a small number of printing pastes prepared from homogenised starch thickenings and these gave prints of good definition and levelness. Pastes which have "set up" during storage will break down under shear but there will be a tendency for the low-stress viscosity to increase again with time and no doubt it is the rate of setting up after homogenising which is of practical importance.

Dr. T. VICKERSTAFF: Can the flow properties of a print paste be altered significantly by varying the

other constituents, e.g. pH, electrolytes, urea, glycerol or oil?

Mr. DERRY: This question is, of course, extremely wide in its scope. Thickenings based on the starches and natural or synthetic gums are often affected considerably in flow behaviour by the other constituents of the print paste. Pastes containing locust bean gum increase very considerably in low-stress viscosity with increase in alkalinity while the alkali sensitivity of gum tragacanth leads to a fall in viscosity on storage. The flow behaviour of thickenings containing a high proportion of carboxyl groups, e.g. the alginates, are susceptible to the influence of divalent cations and this property is made use of in the case of Manutex (Alginate Industries, Ltd.) in order to vary the degree of anomaly of the pastes. Substances forming complexes with the amylose fraction of starch, e.g. pine oil and thymol, improve the flow behaviour of cereal starch pastes by decreasing the low stress viscosity. Certain dyestuffs also associate with the thickening and cause large changes in the degree of anomaly of print pastes.

Mr. D. A. DERRETT SMITH: The effect of the dye on the printing paste is well illustrated by the different degrees of penetration sometimes seen in a printed linen handkerchief cloth.

In a multi-coloured print where the pastes were all made from the same thickening, some colours show satisfactory penetration whereas with others it is often incomplete.

Mr. A. S. FERN: The printing paste must, during transfer, be submitted to a shearing stress which is directly related to the peripheral speed of the printing roller. It is not easy to see why this stress must always be about 4500 dynes/sq. cm. since this would apply equally to very slow and very fast printing speeds. Is it implied that the shearing stress during machine printing is never significantly less than this value?

Mr. DERRY: We cannot agree that the shearing stress must be directly proportional to the speed of printing. If it were so the quality of definition obtained with highly anomalous thickenings should decrease with increase in speed because the apparent viscosity of the paste would be falling. This is not so in practice and therefore other factors must, presumably, determine the rate of transfer. The operative shearing stress would appear to depend ultimately upon the rate at which the fabric and supporting blanket is forced into the engraving and the resistance to flow offered by the compressed fabric in the nip. If the rate of recovery of the fibre-rubber blanket system from elastic compression determines the rate of transfer of the paste then the operative stress may well be constant as implied by the results of these experiments.

Mr. W. J. MARSHALL: First I would like to congratulate the authors on the ingenious way in which they have used the non-Newtonian properties of print pastes to measure shear forces which are not susceptible to direct measurement. In roller printing one would expect the shear force

to which the paste is submitted on being transferred to the cloth to rise as the printing rate increased until a limiting value is reached above which the paste surface is brought against the fibre at a rate so great that the controlling factor is the rate at which the fibre is deformed by the impressed paste. From the authors' observation that the definition is independent of the printing rate it would appear that their experiments were carried out above this limiting rate. This being so the shearing force should depend on the fibre rigidity, the viscosity, and the resilience of the back cloth, knowing the physical properties of the fibre and the back cloth this should be calculable. Immediately arising from this the shear forces should depend on the rigidity of the fibre and the back cloth. Have the authors considered such a picture theoretically or have they observed in practice this type of behaviour?

Mr. DERRY: We would agree that the rate of deformation of the fibre and more particularly that of the underlying backgrey and rubber blanket must be important factors operating in the transfer of paste from engraving to fabric. In addition, the build-up and decay of pressure along the arc of contact in a the nip will also come into the picture as well as the changes in resistance to flow offered by the highly compressed fabric during absorption of the paste. It was because the theoretical approach presented formidable difficulties that the empirical methods described in the paper were devised. We have not carried out any printing trials at very low speeds.

Mr. H. A. TURNER*: Is the extreme drop in apparent viscosity under the intense local pressure of the doctor edge, a reversible effect? I take it that the continuous drop in the apparent viscosity in unstable printing pastes is largely due to the agitation it receives, at relatively low shearing stresses, by the furnishing system. The proportion of paste coming under extreme stress at any one time must be very small, so that it cannot affect very greatly the properties of the bulk of material in the colour box.

Mr. DERRY*: Pastes which are unstable to shear are broken down in the colour box but fortunately the fall in viscosity does not continue indefinitely. After shear breakdown the flow curve becomes reproducible and then the shear-rate thinning taking place under the action of the cleaning doctor is a reversible effect. The main disadvantage of this type of paste is that the equilibrium viscosity at a given shearing stress is dependent not only upon the concentration of thickening, but also upon the conditions of preparation of the paste and it is therefore more difficult to reproduce the flow curve.

Mr. N. B. KATRAK*: It is mentioned that viscosity requirements of the pastes vary with the character of the cloth. Do they also vary with the character of backgrey and blanket?

Mr. DERRY*: We have not determined the effect of the character of the backgrey or blanket on quality of definition. The resilience of the backing may affect the rate of transfer of the paste and therefore the viscosity requirements but it is unlikely to be critical in its influence on the quality of the print.

Mr. J. W. RUWHOF*: In the extension of the preprint article, the authors claimed the shearing stress in doctoring the printing paste to be of the order of magnitude of 10^6 dynes per sq. cm. I should like to know how this was determined.

Mr. DERRY*: It was not intended to imply that the shearing stress operating during cleaning had a clearly defined value. Since the shearing stress is equal to the product of rate of shear and apparent viscosity at the operative rate of shear it will depend upon (a) the clearance between printing roller and doctor knife; (b) the printing speed, and (c) the viscosity characteristics of the paste. If, for example (a) is 0.001 in. (b) 40 yd. min. the rate of shear will be of the order of $2.4 \times 10^4 \text{ sec.}^{-1}$. The shearing stress would then be 10^6 dynes/sq.cm. for a paste of apparent viscosity four poises at this high rate of shear.

* Communicated

Rheology and the Letterpress Printing Process

N. CASSON

Since most printing inks do not obey the Newtonian flow equation, their rheological properties cannot be characterised by a single coefficient of viscosity. However, in the majority of printing inks the shearing stress-rate of shear relation becomes linear at high rates of shear, allowing the flow curve to be defined by two quantities, viz. U the "plastic viscosity" and f the "yield value". The validity and the usefulness of this procedure are discussed. The effects of the U and f values of an ink on its printing performance are considered in outline.

INTRODUCTION

No one who has examined an example of high-quality letterpress printing will deny that it is a product of artistry. There is no doubt that this is as it should be, since the elements of artistic quality defy scientific analysis. On the other hand, the production of such a work of art involves the use of materials, viz. the ink and the paper in the letterpress process, whose properties are the province of science, and it is therefore undesirable that the artist's intuitive judgment should be applied to the assessment and control of these materials. Unfortunately, this appears to have been the case in letterpress printing for many years, the selection and control of inks depending in the main on the judgment of printers of long experience. In the case of printing inks it has been particularly true with regard to flow properties, which have been judged by the sense of touch and occasionally by hearing, when the printer listens to the sound made by a film ruptured between finger and thumb. The necessity both for the existence of such methods and for replacing them by scientific measurements is obvious. Until the science of rheology has advanced to the position where all arbitrary measurements can be replaced by measurements having a fundamental significance, the former are essential. On the other hand, control of existing materials must remain crude and inexact, and the development of new and better materials retarded, until rheological behaviour can be expressed and measured in more fundamental terms.

There are two main reasons why rheology has not been extensively applied to letterpress printing. Firstly, the rheological character of inks is abnormal, and consequently difficult to define precisely; secondly, the mechanism of the passage of the ink through the press is imperfectly understood, and the magnitudes of the various forces, etc. involved are known only very approximately. Consequently a general discussion of these two topics constitutes the main content of this paper.

RHEOLOGICAL CHARACTER OF LETTERPRESS PRINTING INKS

All printing inks consist of solid pigment particles dispersed in some liquid medium, i.e. they are suspensions. From the rheological point of view all suspensions fall into one of two classes—either they obey the Newtonian law of flow, in which case they are referred to simply as *Newtonian*; or they deviate from this law, in which case they are referred to as *non-Newtonian* or are said to exhibit

anomalous flow characteristics. The above is a very general division, and the non-Newtonian group of suspensions is capable of further subdivision depending on the nature of the deviation from Newtonian behaviour.

In more precise terms, when a shearing force of F dynes/sq.cm. is applied to a Newtonian liquid to produce a rate of shear, or velocity gradient, of D sec.⁻¹, it is observed that F and D are related by the equation—

$$F = \eta D$$

where η is the coefficient of viscosity of the liquid, and is constant at constant temperature and pressure. Consequently a knowledge of the value of η gives all the necessary information about the rheological behaviour expected of the material, provided, of course, that temperature and pressure are constant.

Those suspensions which follow the Newtonian law also can be completely characterised by a single viscosity coefficient. This coefficient is always higher than that of the liquid medium, and increases with increasing concentration of the solid phase. Many relationships between η and concentration have been presented, being derived either from theoretical considerations or from experimental results.

The great majority of printing inks are non-Newtonian suspensions, and the relationship $F = \eta D$ does not apply. As mentioned earlier, the deviations may occur in more than one way, and this point is best illustrated by considering plots of shearing force F against rate of shear D (see Fig. 1). Line (ii) is that obtained from a Newtonian material, whilst curves (i), (iii), and (iv) show three ways in which deviation can occur. In the latter three cases the F - D relation is clearly non-linear, and the materials cannot be characterised by a single coefficient of viscosity. Curve (i) is characteristic of materials exhibiting the phenomenon of *dilatancy*. The relation between F and D is linear at low values of D , but at higher values D increases less rapidly than F . Curve (iv) has no linear portion and is obtained from a class of materials known as *pseudoplastics*. Both these types of curve may possibly be obtained by measurements on printing inks, but the great majority of those used in the letterpress process give curves of type (iii). In this type the line shows pronounced curvature at low values of D , and then appears to become linear. This type of behaviour is often referred to as *plastic flow*. In the illustration all the curves are shown passing through the origin; curves of type (iii) can, however, show a definite intercept on the shearing stress axis. The

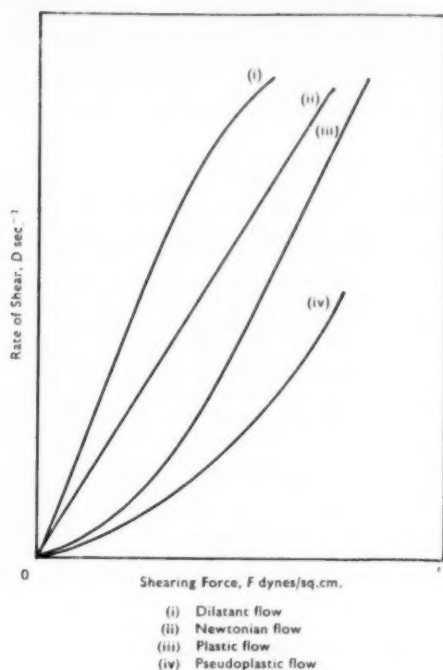


FIG. 1—Types of Flow

basic rheological problem presented by inks can now be seen. Since there exists no unique quantity, i.e. viscosity coefficient, how can the rheological properties be adequately defined and measured? Undoubtedly, the problem could be resolved either by determining the graphical $F-D$ relation over a very wide range of rates of shear, or by measuring the relation at selected rates of shear comparable with those obtaining under practical conditions. However, the first process would be exceptionally tedious, and still severely limited by the rates of shear attainable in laboratory viscometers; whilst the second process requires a fairly exact knowledge of practical conditions, knowledge which is certainly not available in the case of printing. In other words, it is desirable to obtain some mathematical expression for the relation between F and D containing constants which could be used as a measure of the rheological properties of the material.

It has been mentioned that curves of type (iii) are the ones obtained from the majority of inks, and the problems of this case and some attempts at its solution will be discussed in some detail. Firstly, however, it is necessary to mention a further complication, namely the time variation of rheological properties observed in certain cases. If an ink of this type is stirred vigorously, it then has the properties of a fluid and flows easily; but if it is subsequently left to stand at rest, thickening occurs, until the material may eventually appear to be semi-solid. Stirring again regenerates the original fluid character. (In this latter respect it differs from true gelation occurring as a result of some chemical reaction, which cannot be reversed by stirring.) Significant measurements on such materials are

extremely difficult to make, since the properties are continually changing during measurement.

For the sake of simplicity we will consider a material giving a curve of type (iii), typical of printing inks, and assume for the moment that the complication of time variation does not arise. Our problem is to obtain from the experimental data information by which the material can be characterised.

Generally speaking, at the present day, two approaches are made. The first makes use of the concept of *apparent viscosity*, which is defined at any particular rate of shear D as the ratio F/D . The geometry of the $F-D$ curve requires that the apparent viscosity should continually decrease as D increases. In effect this procedure is identical with the one mentioned previously where the $F-D$ curve is taken at its face value and no attempt is made to interpret it through the use of derived constants. Clearly the apparent viscosities of two materials are comparable only if they are obtained at the same rate of shear, and complete information regarding the rheological behaviour of a material can be obtained only by making measurements over a wide range of rates of shear. Provided this is possible, no criticism can be levelled at the method on strictly practical grounds. If a more fundamental understanding of anomalous flow is required for research purposes, however, this method of approach has little to recommend it. Further, it is essential to stress the point that measurements should be made at more than one rate of shear. A considerable number of instruments are available which make "one-point" measurements only, i.e. at one rate of shear. These can give completely misleading results if used to compare materials which in practice are subjected to a range of rates of shear. Fig. 2 shows two hypothetical cases,

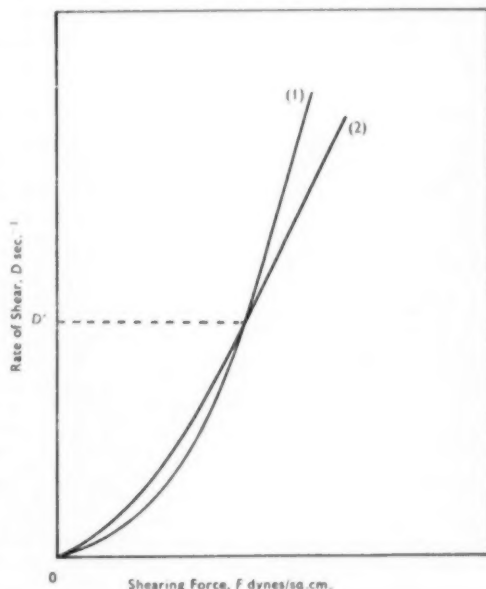


FIG. 2

which, however, could arise in practice. Since the curves cross, the materials have the same apparent viscosity at D' ; above D' sample (1) has the lower apparent viscosity, while the reverse obtains below D' .

The second approach is based on an assumption about the geometry of flow curves of type (iii). When these are obtained by measurements on certain types of viscometer, e.g. concentric-cylinder instruments or cone-and-plate instruments, the curves appear to become linear above a certain rate of shear. If this is the case it is simple to characterise them by two constants, viz. (1) the slope of the linear portion and (2) the intercept obtained by extrapolating the linear portion to the F axis (Fig. 3).

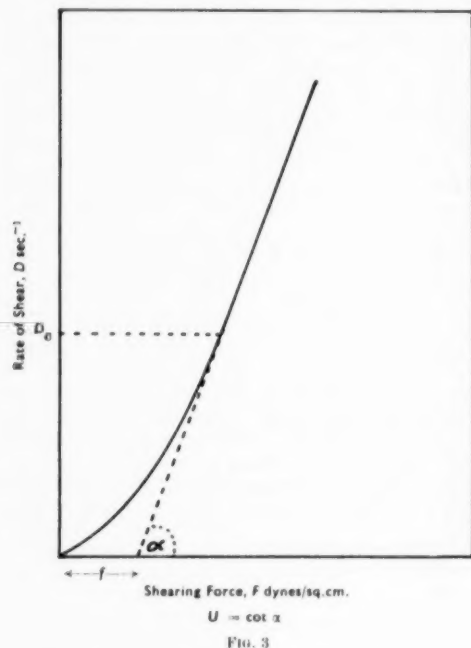


FIG. 3

Such a procedure would appear to be much less valid than the concept of apparent viscosity were it not for the fact that it follows from a reasonable explanation of this type of flow, which further explains the somewhat odd fact mentioned previously that these curves can be obtained only from certain types of viscometer. One mechanism which has been postulated is best illustrated by an experiment carried out by Green¹ on the flow of pigment suspensions through a capillary tube. By a microscopic technique he observed how the pattern of flow varied as the applied pressure was increased. Fig. 4 shows diagrammatically the observations he made. At low pressure P_1 the major part of the material moves bodily as a plug, being lubricated by a thin layer of medium near the walls of the tube. As the pressure is increased (P_2 , P_3), the size of the plug decreases and the remainder of the suspension is sheared. Consequently, it can be concluded that the Newtonian law of flow will not apply until the plug has been completely

eliminated, and anomalous flow effects will certainly arise, since the state of the suspension changes with the applied pressure. According to Green it has been shown that the plug in a capillary tube can be eliminated only by the application of infinitely high pressure.

Green's application of this concept to explain curves of type (iii) (Fig. 1) is based on the assumption that a shearing force f must be applied before shearing begins in a plastic material of this kind, and consequently f must be exceeded throughout the material before all the material shears, i.e. exhibits laminar flow. For shearing stresses above this value it might be expected that Newton's law would apply. It has been said already that in the case of a capillary tube this condition cannot be realised; however, this is not the case in a concentric-cylinder viscometer, or in any instrument where the material is sheared between two surfaces a finite distance apart. In the concentric-cylinder instrument, the outer cylinder, or cup (of radius R_c) is rotated with a constant angular velocity, and the torque M on the inner cylinder, resulting from the flow of the material in the gap, is measured by the deflection of the inner cylinder, which is suspended from a torsion wire. Since equilibrium has been attained, this moment M is constant throughout the material; consequently the force F per unit area, acting on any cylinder of liquid of radius r , will be—

$$F = \frac{M}{2\pi hr^2}$$

(h = depth of immersion of the inner cylinder).

For laminar flow to obtain up to radius r , we have to satisfy the equality $M = 2\pi hr^2 f$, according to Green. The material in the region beyond r will not be sheared, but will rotate with the cup as a solid unit. However, as the speed of rotation of the cup increases M will increase until the equality $M = 2\pi h R_c^2 f$ is satisfied, when laminar flow should obtain throughout the cup and Newton's law should apply. This is the basis of the Green picture of the mechanism of plastic flow producing F - D curves of type (iii): i.e. with rates of shear between zero and the value D_c above which the curve becomes linear (Fig. 3) only part of the material in the cup is being sheared, the remainder moving as a solid unit (*plug flow*). Above D_c the torque is sufficiently high to shear all the material, and consequently laminar flow obtains throughout the material and the flow curve becomes linear. From this picture Green defined two of the constants which characterise the curve: U , the cotangent of the angle α (Fig. 3), having the dimensions of viscosity, was given the name *plastic viscosity*; whilst f , the intercept on the shear stress axis, having the dimensions of force per unit area, he defined as the *yield value*, and according to Green this force must be exceeded at any point in the material before shearing will commence at that point.

It is this last definition which is the weakness of the Green system. The phenomenon of plug flow has been observed experimentally, and there is no doubt that it contributes to the non-linearity of the flow curve at low rates of shear, but the concept of

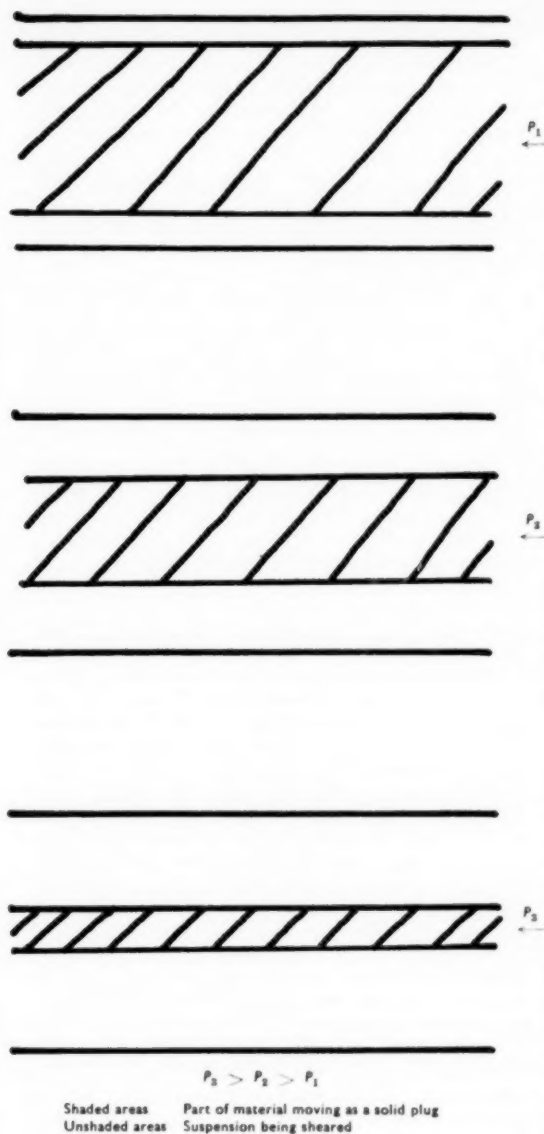


FIG. 4

f as a true yield value cannot explain the shape of the curve. The linear portion follows the law—

$$F = UD + f$$

from which it follows that f is operative at all values of F : i.e. f is a dynamic quantity, whilst Green's concept requires it also to be a simple static yield point. In many cases such true yield points do exist, in which case the curved portion intercepts the shear stress axis at $F > 0$, but in no case can the intercept f be a direct measure of such a quantity.

A more satisfactory explanation of the nature of plastic flow has been reached by consideration of the dynamics of solid particles in a suspension which is being sheared. The starting point for such theories is the assumption that inter-particle

attractive forces exist which can be overcome by subjecting the suspension to shear. Because of these forces, when the suspension is at rest the particles link together to form units known as *floccules*, the process being referred to as *flocculation*. On the application of a shearing force to the suspension these forces are overcome: i.e. the flocculated structure begins to break down. As the shearing stress is increased, more of the floccules break down into smaller units, until eventually no floccules exist permanently. Since the suspension is being sheared, however, particles collide with each other and the inter-particle forces again come into play. In other words, floccules are building up and breaking down simultaneously, and when the shearing stress and the rate of shear become constant both processes must occur at the same rate, since equilibrium has been reached. Consequently, this approach suggests that the character of the suspension changes continuously as the shearing stress F is increased: i.e. the rates of breakdown and build-up are always equal, but the number of floccules present will depend on the value of F . Consequently the relationship between rate of shear and shearing stress will change. Goodeve and Whitfield² have shown that such an approach leads to a flow curve of the same shape as that obtained in practice from plastic suspensions. A similar analysis was carried out later by de Bruyn³. The shape of the plastic flow curve consequently results from the fact that the number of unbroken particle-particle links decreases as F increases. Over the non-linear portion of the flow curve this is occurring rapidly: i.e. the number of links is very high at low values of F . When the curve becomes linear, the number of links remaining is so small that their gradual disappearance with increasing rates of shear virtually leaves the system unchanged. The slope of the linear portion of the curve is now interpreted as the reciprocal of the coefficient of viscosity of the suspension when virtually complete mechanical deflocculation has been achieved, i.e. when floccules exist only for the period of a particle collision, and no floccules exist permanently. The interpretation of the intercept on the shear stress axis is less definite, and depends on the particular theoretical approach made to the process of deflocculation under shear. From a practical point of view this is not important, and since no universal agreement seems to have been reached on this point anyway, the subject will not be pursued further here. The important point is that there is considerable justification for characterising flow curves of type (iii) (Fig. 1) by the slope $1/U$ and the intercept f of the linear portion. Theoretical significance can be attached to the constants U and f , and furthermore they allow the rheological behaviour of the material to be predicted over a very wide range of rates of shear. To avoid confusion in nomenclature, it is desirable to refer to these quantities simply as " U -values" and " f -values".

We have yet to consider the time variation of rheological properties mentioned earlier. This phenomenon is often loosely referred to as *thixotropy*, but once again confusion is likely if this term is used, since it has a different significance for

different rheologists. However, we will use the term here to refer to a significant change in rheological properties with time, when the material is left undisturbed, the change being reversible by the application of a shearing stress. This definition appears to be the most useful when ink behaviour under practical conditions is considered.

Having now obtained a qualitative picture of the rheological character of printing inks and a system by which it may be defined, we are now able to analyse the actual letterpress printing process in rheological terms.

THE LETTERPRESS PRINTING PROCESS

In letterpress printing the areas to be printed are raised above the rest of the plate (Fig. 5A). Consequently the basic requirements for a letterpress

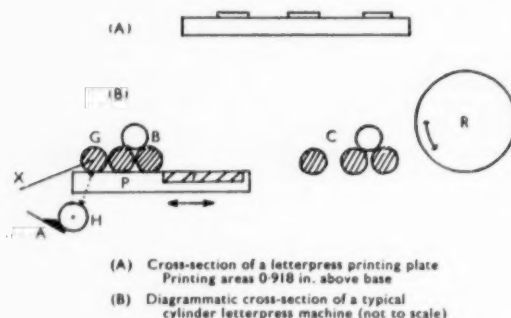


FIG. 5

machine are— (1) an arrangement for applying a uniform film of ink to the area of the plate to be printed, and (2) a means of bringing together paper and printing surface under pressure to effect the transfer of ink from plate to paper.

Fig. 5B shows diagrammatically the layout of a typical flat-bed cylinder machine, details of the paper feed and delivery having been omitted for clarity. The printing process can best be followed by considering the path of ink from the duct *A* to the paper to be printed on the cylinder *R*. The steel roller *H* rotates intermittently, picking up ink from the duct as it does so. The gelatin composition roller *G* is attached by an arm to point *X*, about which it can swivel, and this roller is in contact with *H* whilst the oscillating bed *PF* of the press is at the cylinder end, rising as the bed returns until it makes contact with the plate *P* as shown in the diagram. By repetition of this process ink is transferred to *P*, which is simply a flat metal surface. The ink is now taken from this plate by the first set of distribution rollers *B*. The shaded rollers in the diagram are made of composition, whilst the remainder are of steel. The composition rollers only rotate, but the steel rollers, in contact with those of composition, also oscillate transversely. Consequently in this system the ink is thoroughly agitated. This process is repeated by the similar set of rollers at *C*. These rollers then transfer ink to the printing surfaces in the bed *F* as it passes beneath them. The bed is carried under the cylinder *R*, where it meets the paper under pressure, and the ink is transferred.

Naturally all the processes are carefully synchronised, but the mechanical aspect is of no concern at the moment. Knowing now in outline the treatment the ink receives on its passage through the press, we are able to deduce qualitatively the rheological properties required. The process is usually divided into three stages—

(1) Transport stage— ink transferred from duct to plate.

(2) Distribution stage— distribution of ink on the rollers at *B* and *C*.

(3) Inking and impression stage— ink transferred to plate and then to paper under pressure.

It is assumed that the medium of the ink is capable of wetting both composition and steel; otherwise, of course, no ink transfer would occur at any stage.

Since the roller *H* rotates intermittently and comparatively slowly, the ink in the duct is subject to an intermittent rate of shear which gradually increases towards the bottom of the duct, i.e. as the distance between the duct and roller *H* decreases. The main requirement of the ink at this stage is that it should transfer continuously and at a uniform rate to roller *H*.

Consequently it is essential that the material should flow easily at low rates of shear; in other words, the lower the *f*-value of an ink the better it will behave in the duct. Furthermore, it is very undesirable that the material should possess a true yield point, since then it may not flow down to the roller *H* under its own weight as ink is removed, and the phenomenon of "hanging back" will be observed. This is identical with the plug flow observed in viscometers at low rates of shear. The result of this type of behaviour is a steady loss in colour value in successive prints, and the ink in the duct has to be agitated manually to make it flow down to roller *H*. On long runs thixotropic properties in an ink will lead to similar troubles. Generally the ink structure is broken down manually before the ink is put in the duct, but if the ink is thixotropic it will gradually thicken, since the rates of shear it is subject to are too low to counteract this tendency.

In the distribution stage the conditions are very different. Passing between the rollers, the ink is subject to very high rates of shear, which increase, of course, with the speed of the press. This shearing force is applied only intermittently, viz. when the ink is in the nip between two rollers, and naturally only for a very short period of time. The ink must fulfil two conditions. Firstly it must move smoothly through the distribution system, i.e. transfer evenly from roller to roller; and secondly it must spread out so as to give eventually a film of uniform thickness on the printing plate.

The rheological properties required to permit smooth progress through the roller system are not completely known, since the dynamics of film separation are not fully understood. This aspect will be discussed more fully when the impression stage is considered. Generally speaking, the higher the speed of the press the lower the *U*-value of the ink needs to be. This latter requirement clearly applies to the spreading of the ink to give a uniform film: the lower the *U*-value the more easily will

this be accomplished. However, there is a lower limit, since if the U -value is too low the ink will not distribute uniformly. The question of thixotropy is of little significance in the distribution stage. If the ink is capable of flowing from the duct, which it obviously must do to reach the distribution stage, then no significant build-up will be possible in the latter stage because of the high rates of shear involved. The fact that the shear is intermittent is quite unimportant, since the ink is in the unsheared state only for a very short period of time.

Assuming now that a uniform film of ink has been applied to the printing areas, we must consider the somewhat complex process of transferring the ink to paper under pressure. For this process to be ideal we require that about 50% of the ink on the printing areas of the plate be transferred to the paper, to give an exact reproduction of the printing areas, without damaging the surface of the paper in any way. At the outset it must be emphasised that this process still defies any exact analysis, although a rough qualitative picture has been obtained which allows predictions to be made, generally speaking in agreement with observations.

As the plate and the paper meet, the ink is subject to considerable pressure, this being the greater the smaller the printing area. This pressure has two main effects on the ink—(1) it makes the ink penetrate the pores of the paper, and (2) the ink becomes laterally deformed. The amount of deformation will to some extent depend on (1), since the more easily the ink penetrates the paper the less will be the lateral deformation forces. Obviously, if a true reproduction is to be obtained, lateral deformation must be kept to a minimum. Consequently the ink requires a high U -value, the deformation occurring under a very high pressure. However, a high U -value will tend to hinder penetration into the pores of the paper, and consequently tend to increase the deformation forces, although it is fairly certain that this is not the only factor. Clearly, the nature of the paper is of considerable importance at this stage.

The second part of the impression stage is the separation of plate and paper, and here the somewhat vague concept of ink tack is important. *Tack* can be loosely defined as the resistance of an ink film to rupture. If this quantity is too great, the ink film does not rupture, but the surface of the paper does so. If the paper remains on the cylinder when this occurs, the resulting print is useless, since parts of the printed area have been torn away, a phenomenon known as *picking*. Alternatively the paper may attach itself firmly to the printing plate, being

ripped from the cylinder, and eventually end up among the distribution rollers, from which its removal is a tedious and time-consuming operation.

Many attempts have been made to analyse tack theoretically, and many instruments have been designed to measure it. None of the theoretical approaches appears to be completely satisfactory, although it is generally concluded that the greater the U -value of an ink the greater its tack for a given press speed, tack increasing as press speed increases. From a practical point of view the best method is to measure the strength of ink films under conditions as similar as possible to those obtaining on the press. Conventional viscometry measurements are probably inadequate because of the very high speeds at which forces are applied and the very short times during which they operate. However, it is undoubtedly a rheological problem.

Even when ink has been successfully applied to the paper, the rheological properties are still important in the conversion of the wet ink into a satisfactory dry film. While the ink is wet and still fluid, further penetration into the paper may occur, if the pigment particles in the ink do not form a flocculated structure when at rest. In the absence of such a structure, the liquid medium can gradually soak into the paper, leaving the pigment literally high and dry. As soon as the print is touched smearing occurs. Since f -values are associated with particle flocculation, an f -value is essential to prevent this bleeding away of the medium.

Even from this short account it is clear that the rheological properties of an ink play a very large part in determining the ease with which prints are produced and in determining their quality. At present it is possible to discuss the problem only in general qualitative terms, as has been done here, but a considerable amount of work has been done, and is being done, with the object of clarifying our understanding of such processes as ink transfer. As a result, a more exact and quantitative estimate of rheological requirements will be obtained, leading in its turn to a closer scientific control of letterpress printing inks.

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- ¹ Green, H., *Industrial Rheology and Rheological Structures* (New York: J. Wiley & Sons, 1949).
- ² Goodeve and Whitfield, *Trans. Faraday Soc.*, **34**, 511 (1938).
- ³ de Bruyn, *Rec. Trav. chim.*, **62**, 611 (1943).

Discussion

Mr. J. W. REWHOF: I do not quite agree with the idea of obtaining a mathematical expression for non-Newtonian flow. Not only in many cases a graph tells us quite enough, but there are also quite good viscosimeters obtainable now.

Mr. N. CASSON: Whether or not a mathematical expression is desirable for the characterisation of the flow curve of a non-Newtonian liquid, depends on the type of information required from the

curve. If all that is required is a knowledge of the viscosity of the material over a range of rates of shear then no theoretical expression is needed. On the other hand, any fundamental assessment of the contribution of the components of a system to its viscosity can only be made if the flow curve can be characterised by an equation, containing terms whose magnitude is dependent on the properties of the components.

Mr. RUWHOF: There is evidence (Green p. 218) that Green has not, like you say, had a static but a dynamical conception of yield value, although I admit he is not very clear on this subject.

Mr. CASSON: The main evidence for considering that Green looked upon f as a static yield value is his use of it to explain the non-linear portion of the flow curve of a Bingham plastic material as described in the paper.

Mr. RUWHOF: Not only the rheological properties but also the surface tension may play an important rôle in tackiness, dependent on speed. How is this with textile printing?

Mr. CASSON: It is very interesting to hear that Mr. Ruwhof considers surface tension to be an important factor in tackiness at high press speeds. My own opinion was that surface tension effects would be very small in comparison with other factors but I have not as yet performed any experiments which would confirm or deny this.

Mr. H. WILSON: Can the lecturer give some information of the properties of the printing medium by introduction of gases, commonly resulting in frothing.

Mr. CASSON: The effect of gases in a printing ink, e.g. air trapped during the grinding process and not subsequently expelled, will depend on various factors. Basically a third phase is being introduced in a state of subdivision and an increase in viscosity would be expected. Further, since the "particles" are deformable under shearing stresses their contribution to the viscosity would depend on the rate of shear, i.e. the degree of anomaly would be increased. However, the significance of these effects will clearly depend on the amount of trapped air, and also on the concentration of the

solid phase. If the latter is very high its effects would mask those of the gas.

Mr. A. JOHNSON: As anomalous behaviour occurs only when the solid pigment is added to the ink, it would appear that this behaviour may be due to the two phase system, and possibly to the packing of different sized particles in such a system. Recent work with concrete has shown that the rheological properties can be considerably changed by packing the solids into a very stable state by means of an ultrasonic vibrator. Has the use of ultrasonics been applied to printing inks, and does Mr. Casson think that the rheological properties may be changed?

Mr. CASSON: The anomalous rheological behaviour of solid liquid dispersions, of which letterpress printing inks are an example, is undoubtedly due to the presence of the solid phase in many cases, since measurements on the liquid medium alone show it to be Newtonian. However, it seems unlikely that a "packing" effect is the cause of anomalous behaviour in printing inks since the volume concentration of the solid phase is generally rather too low. However, such an effect would undoubtedly be of importance in a suspension containing a very high concentration of solid. Such a mechanism has been postulated to explain the behaviour of dilatant materials, i.e. the material is in a stable close packed state when at rest, and to make the material flow this state must be disturbed, resulting in an increasing resistance as the rate of flow is increased.

The use of ultrasonics to modify the rheological properties of printing inks is certainly not general and having no experience of the matter I cannot offer an opinion as to what the effect would be. Ultrasonics have certainly been used to prepare dispersions of small particle size.

The Reduction of Vat Dyes in Printing Pastes

W. J. MARSHALL and R. H. PETERS

The relation between the reduction properties of vat dyes measured under conditions akin to practice and their printing properties has been examined. Leuco potentials have been determined from electrometric titrations in aqueous solutions, and they have been found to govern the sensitivity of the dyes to the Formosul concentration.

Complementary to these measurements are those in which the reducing strengths of the pastes have been determined from the potentials developed at a platinum electrode. These results have been related to the leuco potentials of the dyes, and it has been shown that the maximum potentials reached are adequate to reduce all the dyes. Their duration, however, is short for the low concentrations of Formosul and long for the high concentrations. This is due to decomposition of the reducing agent in the presence of gum, and some decomposition rates are given.

The rates of reduction have been measured in print pastes using a model steamer. The times required for complete reduction cover a wide range, but for most dyes they are a substantial proportion of the time allowed for steaming, and must be considered when the printing efficiency of a dye is assessed.

Finally, provided the dye is completely reduced, the maximum fixation is determined by its affinity; rates of diffusion in the fibre, solubility of the leuco dye in the paste, and acid leuco formation do not appear to be important.

INTRODUCTION

The work of Turner and his associates¹ has shown most clearly that the process of printing acid, direct, solubilised vat, and disperse dyes on textile fibres is essentially the same as that of dyeing from a very concentrated dyebath, and there is no reason to suppose that other dyes will behave differently in this respect. With vat dyes, however, dyeing can take place only when the dye is in the reduced state, and since it is present in the print paste initially as the insoluble oxidised derivative, reduction becomes an integral and vital part of the overall vat-dye printing process. In an earlier paper² the present authors measured the reduction characteristics of a number of vat dyes in terms of their rates of reduction and redox potentials, the latter indicating the equilibrium distribution of the dye between its oxidised and reduced forms. In an attempt to correlate these properties with practical printing behaviour, it was observed that the dyes could be divided into two groups according to whether their redox potentials were greater or less than a certain critical value. Dyes of one group all show very poor printing properties, and it was suggested that the critical potential corresponds to the average reduction potential of a Formosul (Br) (sodium formaldehyde-sulphoxylate) print paste, so that these dyes, having more negative redox potentials, are unreduced under normal conditions and hence incapable of printing the fibre. Dyes of the second group have a lower negative potential and are reduced by the print paste, but at a rate determined by their individual chemical and physical characteristics, so that, in general, dyes with the shortest times of half reduction in this group show the best printing properties.

The correlation between these observations and practical printing behaviour was found to be quite good, but the work was admittedly speculative in many respects. In the first place, the reduction properties had been measured under idealised conditions, the redox potentials at 20°C. in anhydrous pyridine for electrochemical reversibility, and the rates in dilute aqueous solution at 40–60°C.,

and could not be properly extrapolated to give the actual time required for the dyes to reduce in the very concentrated aqueous gum print pastes at steaming temperatures. Secondly, the assumption that the observed, critical redox potential corresponded to that of an average potash-Formosul print paste was an inference solely from the printing behaviour. Only a few actual measurements on print pastes were available³, and in any case it is impossible to compare directly the potential of the aqueous print paste system with the redox potentials of vat dyes in pyridine.

Because of these difficulties, it was felt that the further investigations described in the present paper were necessary to place the hypotheses on a more secure foundation. The work involved the measurement of the "leuco potentials" (see below) of vat dyes in aqueous systems, the direct measurement of the reduction potentials of the print pastes under conditions similar to those of practical printing, and the correlation of these observations with printing behaviour. The rates of reduction in a print paste also were measured under steaming conditions. Finally, the influence on printing behaviour of the normal dyeing characteristics of vat dyes, viz. their affinities and rates of diffusion, was examined. The account which follows is divided for convenience into sections dealing with each of these aspects of vat printing.

ELECTROMETRIC MEASUREMENTS ON VAT DYES IN AQUEOUS MEDIA

In ideally reversible oxidation-reduction systems the potential developed at a platinum electrode is defined by the equation—

$$E = E_0 + \frac{RT}{nF} \ln \frac{[\text{Ox}]}{[\text{Red}]} \quad (i)$$

(E = measured potential; E_0 = redox potential of the dye; $[\text{Ox}]$ and $[\text{Red}]$ = molar concentrations of oxidised and reduced dye respectively; R = gas constant; T = absolute temperature; F = the faraday; and n = number of electrons involved in the reduction). In the case of a vat dye in alkaline aqueous solution, the oxidised form is very sparingly soluble. Consequently, if a fully reduced solution is

gradually oxidised, the oxidised dye separates out in the solid state at a very early stage in the process, and $[Ox]$ is thereafter constant and equal to the solubility $[Ox]_{sat}$ of the dye in water. Also, the electrode reaction is not always reversible. Thus—

$$E = E_0 + \frac{RT}{anF} \ln [Ox]_{sat} - \frac{RT}{anF} \ln [Red]$$

$$= E_0 - \frac{RT}{anF} \ln [Red] \quad (ii)$$

where α is a measure of the reversibility of the reaction, being unity in ideal cases.

In order to determine the standard redox potential of a vat dye, therefore, the technique ideally involves the gradual oxidation of a solution of the leuco dye accompanied by determination of the platinum electrode potential and the concentration of remaining leuco compound at each stage. From these values and the solubility of the oxidised dye it should be possible to calculate E_0 .

Unfortunately, in practice the solubilities of the dyes are not known, and would be very difficult to determine; while the work of Geake and his coworkers⁴ has revealed additional difficulties. For instance, the solution may become supersaturated

can be used to compare different dyes and reducing agents. Geake determined the "mid-point potential", i.e. the potential obtained when a leuco solution of specified initial concentration has been half oxidised. A more satisfactory criterion is the "leuco potential" suggested by Lincken, Grand, and Fordemwalt⁵, which is defined here as the potential developed when a solution of the leuco dye is oxidised to the point at which it is just saturated with the oxidised form (represented by E_0 in equation (ii)). In the present work, this has been found to be the most easily reproduced part of the titration curve.

In order to determine these potentials experimentally, complete titration curves have been determined with aqueous solutions of the vat dyes reduced initially with a slight excess of sodium hydrosulphite and reoxidised with potassium ferricyanide. Reduction, and titration with the oxidising agent, were carried out in absence of air at 60°C. (except for the indigoid and the thioindigoid dyes, with which a higher reduction temperature of 80°C. was employed, the temperature being subsequently lowered to 60°C.). The potential of the solution was determined at each stage in the oxidation by means of a platinum electrode and an external saturated calomel half-cell, the latter being maintained at 20°C. In the case of three of the dyes—Caledon Yellow GN, Caledon Jade Green XN, and Durindone Red B—confirmatory titrations using catalytic reduction of the dye and also a direct reduction titration with sodium hydrosulphite gave results consistent with the standard technique. Typical curves obtained by the normal method are shown in Fig. 1. The curves are all of roughly the same shape, starting at the very negative potential of the reducing agent and then rising suddenly to the "leuco potential" of the dye when the excess of sodium hydrosulphite has been oxidised. Further oxidation leads only to a very gradual increase in potential, the curve being almost horizontal in this region, until nearly all the leuco dye has been oxidised, when there is again a very rapid rise in potential.

The titration curves of vat dyes differ to a greater or less extent from the behaviour which would be expected of an ideal dye having an insoluble quinone, and the extent of the deviation from ideality can be assessed by means of two factors, namely the value of α (the reversibility) and secondly the total titre of oxidising agent needed to oxidise the dye. In nearly all cases α was found to deviate from unity, as will be seen from the results given in Table III, while the titres differed by about 25% from the theoretical value. Five dyes, however, gave curves with $\alpha = 1$ and the correct titre, and the leuco potentials of these dyes are compared with the redox potentials in anhydrous pyridine² in Table I. It will be seen that the two methods of measurement not only place the five dyes in the same order but also give potentials which differ by approximately the same amount throughout the series. This constant difference is due to the method of calculating the leuco potentials (equation (ii)) and the difference between the reference electrodes,

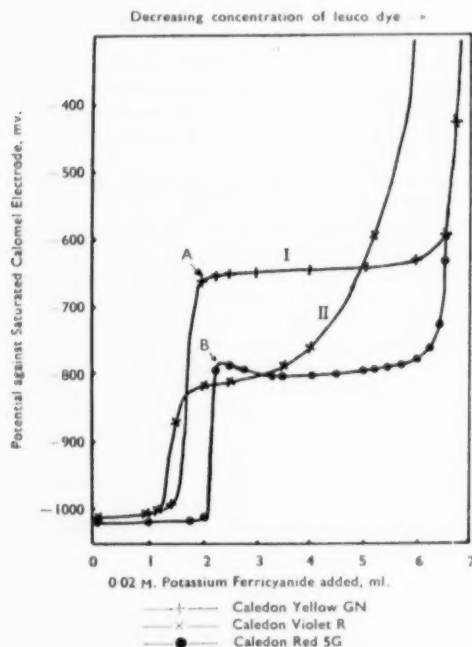


FIG. 1—Typical Titration Curves of Leuco Vat Dyes in Decinormal Sodium Hydroxide Solution at 60°C.

with oxidised dye (B, Fig. 1), the potentials at the electrode may not be truly reversible, over-reduction may occur, and the occurrence of semi-quinones may cause the titration curve to split up partly or completely into two steps (curve (ii), Fig. 1). Under such conditions there is little practical value in attempting a detailed analysis of the oxidation titration curve, and the best procedure is to try to determine some characteristic and reproducible aspect of the reduction which

Thus these experiments confirm that, for dyes which behave ideally in aqueous solution, the ease of reduction can be expressed either by the redox potential in pyridine or by the aqueous leuco potential. Since, however, the great majority of the dyes show considerable deviations from ideal behaviour, it is probably better to assess reducibility in terms of leuco potential, on the assumption that this potential will be a better indication of the behaviour of the dye in an actual print paste.

TABLE I
Comparison of Redox Potentials in Pyridine with Leuco Potentials in Aqueous Solution

(Dye concn. for leuco potentials = 5×10^{-4} M.)

Dye	Leuco Potential (mv.)*	Redox Potential (mv.)†	Difference (mv.)
Caledon Red 5G	-807	-402	405
Caledon Pink RL	-752	-373	379
Caledon Red BN	-704	-247	457
Caledon Yellow GN	-655	-229	426
Durindone Red B	-612	-164	448

Mean difference ... 423

* Against external saturated calomel electrode

† Against Ag/AgNO₃ electrode

Since the leuco potential is the most reproducible characteristic of the titration curve, it is interesting to compare the results obtained in the present investigation with those reported by Lineken *et al.*⁵ and by Geake *et al.*⁴. The results for the four dyes for which comparison is possible are shown in Table II. Again all three measurements place the

TABLE II
Leuco Potentials and Midpoint Potentials

Dye	Leuco Potentials (mv.)			Midpoint Potentials (mv.)
	(a)*	(b)*	(a) - (b)	
Pyranthrone	-950	-892	58	-660
Dibenzanthrone	-900	~-840	60	-640
Caledon				
Jade Green XN	-875	-815	60	-575
Flavanthrone	-770	-655	115	-233

* (a) Lineken *et al.*⁵; (b) this work

dyes in the same order, while there is reasonably good agreement between the two sets of leuco potentials. (The differences in the absolute values of the potentials are probably due to the different reference electrodes employed and the different conditions of measurement.) The leuco potential thus appears to be a satisfactory characteristic of the aqueous vat dye system. The comparisons must be made at the same molar concentration of the dyes (equation (ii)). Accordingly the leuco potentials of a wide range of dyes have been determined (Table III),⁶ all experiments having been carried out with 5×10^{-4} M. dye solutions. The leuco potentials were determined from the titration curve by extrapolating the steeply rising and the horizontal portions to the point of intersection.

In the previous work² the redox potentials of vat dyes were compared with the "ease of printing". For this purpose a series of patterns were printed

TABLE III
Comparison of the Reduction Potentials of Vat Dyes with their Printing Properties

Dye	Leuco Potential (mv.)	Reversibility of Reaction (a)	Critical Formosul Concn. in Potash Print Paste (%)
Caledon Gold			
Orange G	... -892	0.22	-
Caledon Brown R	-878	1.07	7
Caledon Yellow 4G	-859	0.66	-
Caledon Brilliant			
Red 3B	... -850	1.03	6
Caledon Red X5B	-870	0.22	-
Caledon Yellow 5G	-842	-	5
Caledon Brilliant			
Purple 4R	... -835	1.00	2
Caledon Printing			
Brown 4R	... -830	0.27	5
Caledon Brilliant			
Violet R	... -817	0.19	6
Caledon Jade			
Green XN	... -815	0.52	2
Caledon Red 5G	... -807	0.96	-
Caledon Blue GCP	~-800	-	1
Durindone Brown G	-757	0.81	2
Durindone Orange R	-752	0.61	-
Caledon Pink RL	... -752	1.03	-
Durindone Pink FF	-725	0.61	2
Caledon Brilliant			
Orange 6R	... ~-709	-	1
Caledon Red BN	... -704	1.10	0
Durindone Scarlet Y	-671	0.73	2
Caledon Yellow GN	-655	1.18	0
Durindone Blue 4BC	-646	0.17	0
Durindone Red 3B	-615	0.59	0
Durindone Red B	-612	1.07	-

with various Formosul concentrations and steamed for various times, and were then mounted in the form of a rectangle in order to demonstrate the build-up of colour with these two variables. Efficiency of printing was judged by the uniformity of colour over the whole block. Now, with the more detailed analysis of printing carried out by Michie and Thornton⁶, a more logical comparison can be made between the leuco potentials and the sensitivity of the dyes to Formosul concentration in the print paste. These authors have plotted the amount of dye fixed in printing against the concentration of Formosul in the paste, and have found that the fixation varies enormously over a small range of concentrations, the final curve being S-shaped, as is shown by the examples in Fig. 2. Dyes which can be reduced at low Formosul concentrations do not give the complete curve (i), Fig. 2), and hence to avoid ambiguity the sensitivity of the dyes to Formosul has been defined as that concentration required to give 50% of maximum dye fixation. If the fixation is greater than 50% in absence of Formosul the concentration is assumed to be zero. These Formosul values are given in the last column of Table III, and show on the whole a good correlation with the leuco potentials, thus confirming that this potential is a satisfactory indication of the relative ease of reduction of vat dyes in an aqueous system.

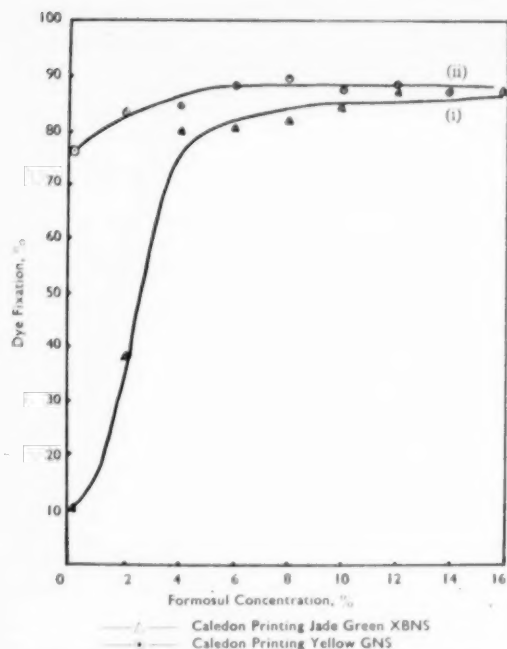


Fig. 2—Effect of Formosul Concentration on the Percentage of Dye Fixed after Steaming for 8 min.

REDUCING PROPERTIES OF PRINT PASTES

To complete the picture of the reduction process, some knowledge of the reducing power of the various reducing agents, including the printing gums, is essential. For a reversible system, this reducing power can again be measured by the electrical potential developed at a platinum electrode. If the leuco potentials of the vat dyes and the reduction potentials of the reducing agents are both measured against the same reference electrode, so that they are on a common scale, then a reducing agent must develop a potential at least equal to the leuco potential of a dye in order completely to reduce the latter.

Unfortunately the potentials developed by the reducing agents used in practice are not reversible, and for this reason some preliminary measurements were made on aqueous solutions in order to investigate the significance of the measured potentials before turning to the examination of reducing agents in print pastes. The forms of apparatus used for the solutions and for the print pastes were slightly different.

For the examination of solutions, the apparatus was similar to that employed in the determination of the titration curves of the dye. The cell contained an alkaline solution of the reducing agent, but the platinum electrode was not introduced until this solution had reached the temperature of the thermostat (60°C.). The potential was then followed as a function of time, measurements being taken at 5-min. intervals.

Some typical potential-time curves are given in Fig. 3 and show that a substantial period of time is necessary before constant readings are obtained. This sort of behaviour is to be expected for

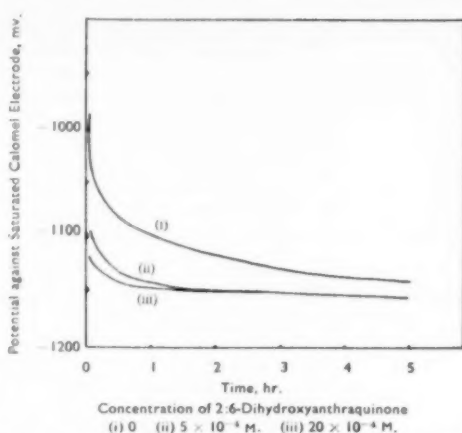


Fig. 3—Effect of 2:6-Dihydroxyanthraquinone on the Rate at which an Electrode reaches a Steady Potential (20 g. NaOH + 20 g. $\text{Na}_2\text{S}_2\text{O}_4$ per litre at 60°C.)

irreversible systems, but it is significant that the results are reproducible (to within ± 10 mv.). Furthermore, although addition of potential mediators (e.g. 2:6-dihydroxyanthraquinone) speeds up the rate of attainment of the steady value as indicated in Fig. 3, such addition does not alter the final value obtained, a fact which lends support to the view that the final potentials are a true reflection of the reducing power of the agents. Some of the results are given in Table IV, from which it will be seen that at 60°C. Formosul is a weaker reducing agent than sodium hydrosulphite.

TABLE IV

Equilibrium Potentials of Reducing Agents

(0.11 N. Reducing agent + 0.5 N. NaOH at 60°C.)

Reducing Agent	Additive	Potential (mv.)
Sodium hydrosulphite	None	-1137
	0.0005 M. 2:6-Dihydroxyanthraquinone	-1153
	0.04 M. 2:6-Dihydroxyanthraquinone	-1150
	0.001 M. Alizarin	-1144
	0.001 M. "Silver salt"*	-1133
Formosul	None	-1037
	0.001 M. "Silver salt"*	-1037

* Sodium anthraquinone- β -sulphonate

With very dilute solutions of reducing agent, slight differences in potential are produced by the addition of mediators, but since concentrated solutions are employed in practical printing, this is of little significance.

On comparing these potentials with the leuco potentials of the dyes (Table III), it will be observed that Formosul in presence of caustic soda should be capable of reducing all the dyes. To test this observation, eleven dyes were selected, and it was found that in fact reduction with Formosul did occur, although the rates of reduction were very low. Nevertheless, this did confirm that the reduction potentials measured in this way may be regarded as a true indication of the reducing power of the agents and a guide to their ability to reduce vat dyes.

The next step was to measure the reduction potentials of actual print pastes, and for this purpose a rather different apparatus was constructed. The time required for these measurements was considerable, so that arrangements were made to record the potentials automatically. Six samples were examined at one time, each contained in a stoppered glass test-tube cell, which was filled to the bung to exclude air and immersed in a thermostat containing liquid paraffin. Platinum electrodes in each cell were connected to an automatic selector switch and thence to a direct-reading pH-meter. As the switch rotated, each cell in turn was connected to the meter and its potential was recorded. All cells were connected by salt bridges to a common external (saturated calomel) reference electrode. By this means it was possible to obtain a

continuous record of the potential of a paste sample for periods up to 24 hr. with an accuracy of 3–4 mv.

The rise and decay of the reducing power of typical print pastes (based on potash-Formosul) as a function of time are illustrated in Fig. 4. In this diagram, reducing power increases with increasing negative potential. It will be seen, therefore, that all the pastes first increase very rapidly in reducing power, and then after a certain interval the reducing power decreases, finally reaching the value due to the printing gum alone. The maximum reducing power and the length of time for which this is effective increase with increasing Formosul concentration. At very low concentrations effective reducing action is merely transitory, whereas at high concentrations it is maintained over a long period. These observations, of course, apply only to the anaerobic conditions employed in these experiments. With the more powerful sodium hydrosulphite, similar curves were obtained, but with a higher maximum reducing power and a rate of decay about 30 times as rapid as with Formosul.

The effects of some variations in the other components of a print paste are shown in Fig. 5. Formosul is a more active reducing agent in presence of caustic soda than of potassium carbonate, but is correspondingly less stable. The effect of temperature is not marked. The results for a wide range of print paste formulations are presented in Table V arranged in order of their reduction potentials. In considering these results, however, it must be emphasised that it is not the potential alone which determines practical reducing power, but also the length of time for which the potential is maintained. It appears probable that the decrease

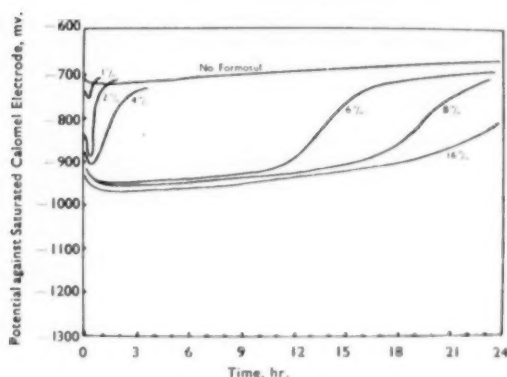


FIG. 4.—Typical Curves for the Rate of Change of Potential for Potash-Formosul Printing Pastes at 98°C. with Various Concentrations of Formosul, illustrating their Relative Reducing Powers

TABLE V

Effect of Composition of Print Pastes on Reduction Potentials

Temp. (°C.)	Glycerol (%)	Thickener	Alkali	Reducing Agent	Minimum Potential achieved (mv.)
98	5	(Water)	13.5% K_2CO_3	—	(Unstable)
98	—	Gum tragacanth	13.5% K_2CO_3	—	-710
98	5	Gum tragacanth	13.5% K_2CO_3	—	-720
98	5	British gum	13.5% K_2CO_3	—	-724
98	5	British gum	13.5% K_2CO_3	1% Formosul	-757
80	—	(Water)	Na_2HPO_4	1.3% Formosul	-821
(A) Lowest reduction potential required to reduce all the vat dyes					
90	5	British gum	13.5% K_2CO_3	2% Formosul	-896
98	5	British gum	13.5% K_2CO_3	4% Formosul	-910
98	5	British gum	8% NaOH	—	-935
98	5	British gum	13.5% K_2CO_3	6% Formosul	-950
98	5	British gum	13.5% K_2CO_3	8% Formosul	-960
80	—	(Water)	0.5 N- K_2CO_3	1.3% Formosul	-967
98	5	British gum	13.5% K_2CO_3	1.6% Formosul	-972
98	5	Gum tragacanth	13.5% K_2CO_3	8% Formosul	-980
98	5	British gum	8% NaOH	2% Formosul	-980
98	5	(Water)	13.5% K_2CO_3	8% Formosul	-1010
98	5	British gum	13.5% K_2CO_3	8% $Na_2S_2O_4$	-1025
80	5	British gum	8% NaOH	2% $Na_2S_2O_4$	-1030
80	—	(Water)	0.5 N-NaOH	1.3% Formosul	-1061
98	5	British gum	8% NaOH	8% Formosul	-1082
60	5	(Water)	0.5 N-NaOH	2% $Na_2S_2O_4$	-1140
80	5	(Water)	8% NaOH	8% $Na_2S_2O_4$	-1153

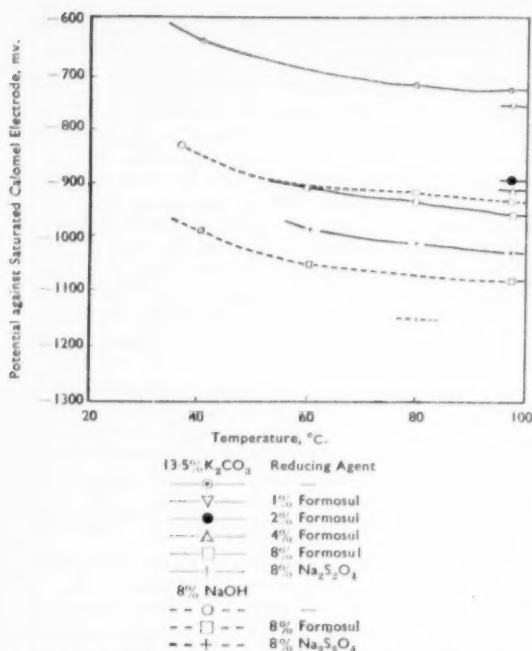


Fig. 5—Reduction Potentials of Printing Pastes based on British Gum, showing the Effects of Temperature, Alkali, and Reducing Agent

in reducing power with time is due to decomposition of the agent, as will be shown later.

To facilitate comparison of these results with the reduction properties of the vat dyes, a line *A* has been drawn across the table corresponding to the potential of the dye which is most difficult to

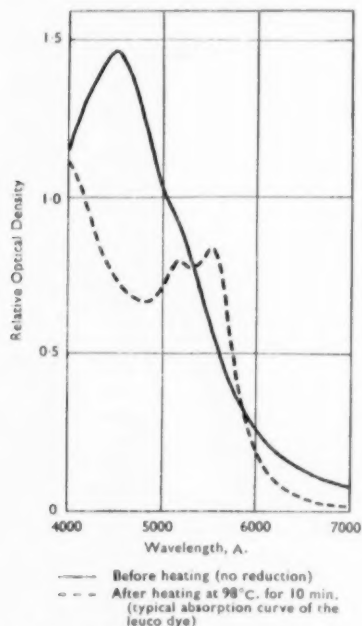


Fig. 6—Reduction of Caledon Printing Orange G8 in a British Gum Print Paste containing Sodium Hydroxide but No Added Reducing Agent

reduce. All systems lying below this line should be capable of reducing all the vat dyes tested. It will be seen that this includes almost all the formulations likely to be encountered in practice and even British gum in presence of caustic soda. To check this point, Caledon Printing Orange G, a dye with a very negative leuco potential (-892 mv.), was reduced by a paste of British gum and caustic soda after being heated for 10 min. at 95°C . The change in absorption spectrum is shown in Fig. 6. In accord with the potentials, also, British gum was found not to reduce this dye in the presence of potassium carbonate. Finally, in agreement with practical experience, a paste of potassium carbonate and British gum with a potential of -720 mv. was found to be capable of reducing a substantial number of dyes, such as the Durindones, with less negative leuco potentials.

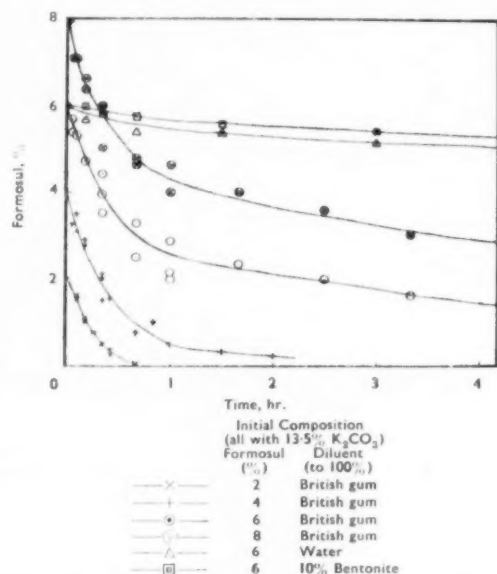


Fig. 7—Rates of Decomposition of Formosul at Various Concentrations with and without British Gum

The results do lead to one important conclusion, namely that, although the minimum potentials of the print pastes containing Formosul are sufficiently negative to reduce all the dyes discussed here, the lower concentrations do not do so, owing to the decomposition of the reducing agent, as indicated by the short interval of time during which the "minimum" potential is maintained.

In order to examine this point in more detail, experiments were carried out to determine the rate of decomposition of Formosul in print pastes. A number of small hypodermic syringes were filled with the paste and stoppered at the needle end to exclude air, expansion being taken up by movement of the piston. The syringes were immersed in a thermostat at 98°C ., and after the requisite period of time had elapsed the paste was ejected into a 2% formaldehyde solution. The Formosul was estimated in the usual way by titration with standard iodine and sodium thiosulphate solutions.

The amount of Formosul present in the paste was plotted as a function of time, a selection of the rate curves so obtained being given in Fig. 7.

The rate of decomposition was found to depend on the initial concentration, being relatively more rapid for the more dilute solutions. For example, the concentration of a paste initially containing 6% of reducing agent decreased to 2% after an hour, but the subsequent decomposition of this remaining 2% took place at a considerably lower rate than that of a paste with an initial concentration of 2%. This retardation is perhaps due to the accumulation of decomposition products such as formaldehyde or formaldehyde-bisulphite. Both these compounds when added to a paste decreased the decomposition of Formosul. Under practical conditions in a steamer, volatile products such as formaldehyde will be quickly removed from the paste, and it seems certain that decomposition will occur at a considerably greater rate than in the experiments described here. It may be noted also that in the absence of gum the decomposition was considerably less. These results therefore elucidate the paradox that, although the reduction potential indicates that a low Formosul concentration should be adequate to reduce all the vat dyes tested, in actual fact it is found to be incapable of doing so. The success or otherwise of the reduction in the paste depends on the relative rates at which the dye is reduced and at which the reducing agent is decomposed.

RATES OF REDUCTION OF VAT DYES IN PRINT PASTES

By measuring the rates of reduction of a series of vat dyes in dilute aqueous suspensions, the present authors² were able to show that those dyes which reduced very slowly gave unsatisfactory prints, and it seemed from these observations that the time necessary to reduce the dye must be an appreciable fraction of the total steaming time.

However, these rates had been measured at temperatures of 40° and 60°C., and preliminary experiments at higher temperatures, still using the aqueous caustic soda-hydrosulphite system, indicated that the rates of reduction of all the vat dyes tested were extremely high, so that reduction should be practically instantaneous on steaming at 100°C. If, therefore, the rate of reduction is really an important factor in printing, as suggested in the earlier paper, then reduction in a print paste must be a much slower process than in aqueous solution. Consequently, it was thought essential to study the rate of reduction of the dyes in an actual print paste composition containing Formosul and potassium carbonate under true steaming conditions.

In the experimental technique used for this purpose, a model steamer (Fig. 8), designed to fit into the cell compartment of the Carey recording spectrophotometer, consisted of a tall Pyrex beaker fitted with a Tufnol lid with a rubber seal, through which the sample could be introduced. The lid

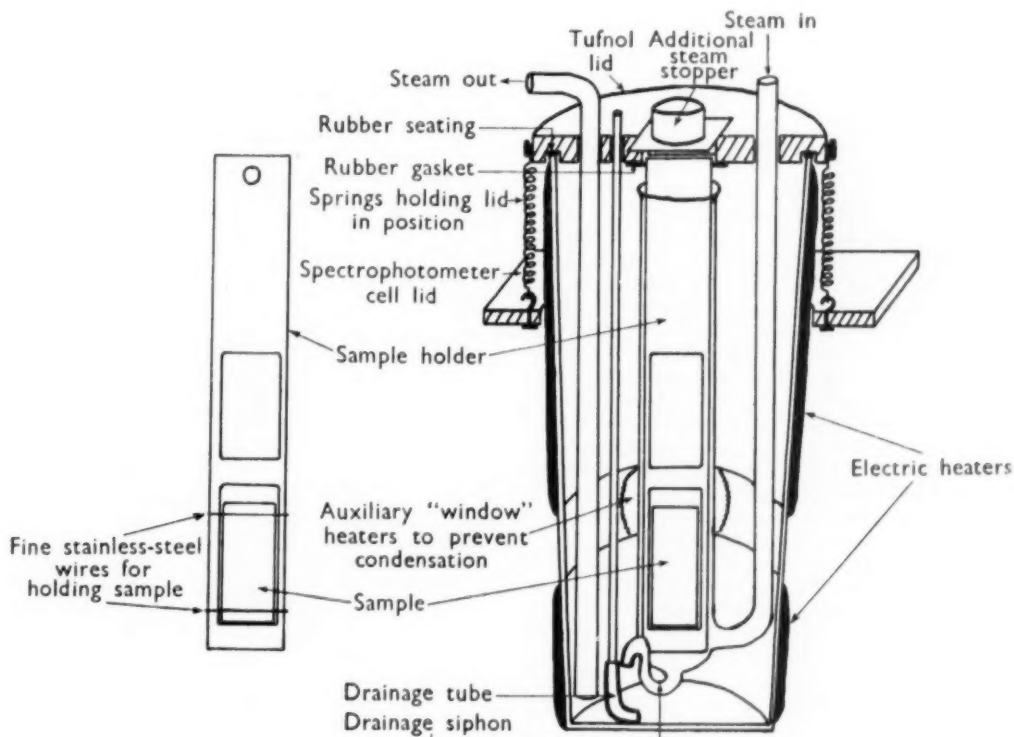


FIG. 8—Diagrammatic Arrangement of Steamer

supported also an inner concentric glass tube $1\frac{1}{2}$ in. in diameter, which formed the actual steaming chamber. Steam was generated in a flask, passed through a drying coil, and introduced into the bottom of the outer jacket. After circulating through the annular space, it entered the inner compartment, and finally escaped through the exit tube. The sample to be examined was placed in a Tufnol holder, which slipped into the inner tube. The beaker was heated electrically over as much of its external area as practicable, and boost heaters were fitted around the "windows" to prevent condensation from interfering with the passage of light. The rates of reduction were followed by the changes in optical density of the sample. On starting up, although the apparatus quickly attained a temperature of 100°C ., showing the air to be rapidly displaced, steam was passed for an hour prior to measurements being made.

Printed cloth was found to be unsuitable for these experiments, because the light beam of the spectrophotometer merely passed through the interstices of the fabric and was not absorbed by the dye. Hence samples were prepared by coating a print paste mixed with 10% cellulose powder to a thickness of 0.003 in. on a glass lantern slide, cut to the correct size for the holder. The samples were dried at 70°C . for 15 min. before being steamed. With this system, changes in the light absorption characteristics of the dyes during reduction could be measured. One difficulty which was encountered was apparently due to the fact that the sample did not have the moisture uptake of cloth, so that some

condensation on the slide occurred, which interfered with the optical measurements. This was finally overcome by preheating the sample and adjusting the temperature of the steam by means of the drying coil. The rates of reduction under such conditions compared very well with estimates obtained visually using printed cloth and normal steaming.

Each experiment was carried out in duplicate, agreement between the two runs being satisfactory in most cases. Unfortunately it is not possible to specify the overall accuracy of these experiments, since this depends on the differences in absorption spectrum of the leuco and oxidised forms of the different dyes. If the differences were large, measurements were simple, whereas with other dyes the small differences in optical density between the oxidised and reduced forms necessitated great care in order to obtain results of reasonable accuracy.

The printing pastes which were used had the following composition—

13.5%	Potassium carbonate
5%	Glycerol
1-6%	Dye (according to the intensity of the leuco colour)
8%	Formosul (unless otherwise stated)
	British gum.

The materials were of technical quality and the dyes the normal printing brands, pastes fine, or pastes (in that order) according to availability.

The results are given in Table VI, where the rates in the pastes are compared with those

TABLE VI
Rates of Reduction of Vat Dyes in Print Pastes

No.	Dye	Dye Concn. in Print Paste (%)	Time for 50% of Max. Reduction in Print Paste (sec.)	Time for 50% of Max. Reduction in NaOH-Na ₂ S ₂ O ₄ (sec.)	Time to reach 80% of Max. Fixation (sec.)
1	Caledon Printing Yellow GNS ...	1	5	<5	270
2	Caledon Printing Red BNS ...	1	8	<5	220
3	Durindone Printing Blue 4BCS ...	1	10	—	—
4	Caledon Navy Blue 2RS paste fine ...	3	12	31	—
5	Caledon Printing Orange 6RS ...	1	20	—	330
6	Caledon Printing Jade Green XBNS ...	2	25	43	236
7	Durindone Printing Brown GS ...	1	30	780	450
8	Caledon Printing Orange GS ...	2	34	36	—
9	Caledon Yellow 4GS paste fine ...	3	35	27	—
10	Durindone Printing Red BS ...	1	36	113	—
11	Caledon Printing Jade Green XN 200 ...	1	44	50	—
12	Caledon Printing Yellow 5GS ...	3.5	45	—	900
13	Durindone Printing Red 3BS ...	1	50	—	660
14	Caledon Brilliant Purple 4R 150 paste fine ...	2	60	—	440
15	Caledon Pink RL200 paste fine ...	4.5	60	181	—
16	Caledon Brilliant Violet RS paste fine ...	6	65*	33	510
17	Caledon Printing Red ³ B 200 ...	3	75	291	450
18	Durindone Printing Scarlet 3BS ...	1	80	—	—
19	Durindone Printing Pink FF 125 ...	2	88	2880	690
20	Caledon Brown RS paste fine ...	3	90	27	400
21	Durindone Printing Scarlet YS ...	1	100	—	660
22	Durindone Printing Orange R 150 ...	2	110	3000	—
23	Caledon Red 5GS paste fine ...	1.5	110*	503	—
24	Caledon Red X5B paste fine ...	3	280	390	—

* These print pastes appeared to be incompletely reduced even after maximum reduction had been achieved

previously measured at 40°C. in aqueous caustic soda-sodium hydrosulphite solutions (20 g. of each per litre). In the final column are recorded the times required to reach 80% of maximum fixation of the dye on the cloth as measured by Michie and Thornton⁶. This comparison shows that fixation is apparently determined to some extent by the rate of reduction in the paste, although the range of times required for fixation is narrower. It should be especially noted that some of the discrepancies between the two series of measurements arise from the use of printing-quality dyes as compared with the paste brands used in the aqueous measurements; for example, Durindone Printing Brown GS reduces more quickly than would be inferred from measurements on Durindone Brown GS paste at the lower temperature.

It was found that the rate-of-reduction curves were not always of the same shape, but even so, the major part of the reduction was complete after a period three times as great as the time necessary for 50% reduction, and this value ($3t_{0.5}$) has been taken as a convenient measure of the time of reduction. Approximately half the dyes examined had reduction times of 180 sec. or more—an appreciable and sometimes considerable proportion of the ageing time commonly employed in practice, which may vary from 300 to 600 sec. The rate at which a dye fixes must therefore depend on its rate of reduction, and in general dyes with low rates of reduction will require longer times of fixation. Further, even when the dye has been reduced, a certain time is required for transfer from the paste to the fibre; for example, Caledon Printing Yellow GNS is reduced in a few seconds and yet needs 270 seconds to attain 80% fixation. In general, it appears that vat dyes have times of fixation which exceed the time required for reduction by 150–770 sec.

To summarise the results of this section of the investigation, it has been shown that the rates of reduction of vat dyes in a typical print paste on steaming are much lower than would be anticipated from the behaviour of the dyes in aqueous suspensions. At least part of this difference arises from the differences in the reducing system, for Formosul reduces dyes very slowly as compared with sodium hydrosulphite at temperatures below 100°C., while the replacement of caustic soda by potassium carbonate also retards reduction, as shown by the typical results of Table VII.

TABLE VII
Effect of Potassium Carbonate on the Rates of Reduction of Vat Dyes

Dye	Time for 50% Reduction	
	0.5 M-NaOH (sec.)	0.5 M-K ₂ CO ₃ (sec.)
Caledon Red BN ...	5	12
Caledon Brilliant Violet R ...	33	50
Caledon Jade Green XN ...	50	270
Caledon Pink RL ...	181	260
Durindone Red B ...	184	684

The long times needed for the reduction of vat dyes in print pastes, being comparable with the total steaming times, are therefore an important factor in determining printing behaviour, and a

high rate of reduction is a very desirable characteristic in a vat dye for textile printing. It does not necessarily follow, however, that all dyes which reduce rapidly will be suitable for printing, for other factors, such as affinity and the transfer of dye from paste to fabric, may affect the degree of fixation finally achieved with any particular dye.

DYEING FACTORS

Attention has so far been devoted to assessing the importance of the reduction step in determining printing properties. However, provided this part of the process is successful, the transfer of the dyes from paste to fibre must depend on other properties, presumably similar to those governing normal dyeing. For vat dyes the following points need clarification—the state of the leuco dye in the print paste, the rate of diffusion of the dye through the paste and the fibre, and finally the affinity of the dye for the fibre. With regard to the first of these factors, one of two difficulties may arise to slow down the transfer—the formation of an insoluble acid leuco derivative of the dye or the precipitation of the potassium salt of the leuco dye owing to low solubility in the highly concentrated solution of electrolytes in the print paste.

Since there is a marked change in the spectra of vat dyes when the ionised form is converted to the acid leuco compound, the absorption spectra obtained incidentally to the rate-of-reduction measurements were studied. These indicated that with every dye examined the fully ionised leuco form was present in the paste. This was checked by reducing the dyes in the presence of buffers of varying pH, when it was found that at the pH values given by potassium carbonate solutions complete ionisation could be expected.

The second alternative of precipitation of a potassium salt is more difficult to examine. Solubilities of these compounds are extremely difficult to measure owing to the masking of precipitation by the intense colour and to the great ease of oxidation. Some qualitative information was obtained as follows—Small amounts of the dyes were reduced in a solution of potassium carbonate (13.5%) and Formosul (8%) in the absence of air. At the boil (107°C.) the dyes gave clear solutions, but on cooling they were precipitated. Under conditions more akin to printing, a solution of 13.5 g. of potassium carbonate in 31 g. of water (31.2% being the amount of moisture present in the print paste after being steamed for 10 min.) was used for reduction, when it was found that at the boil some dyes were insoluble, but that even these gave clear solutions on the addition of 5 g. of glycerol. Since glycerol is often present in pastes used in practice, it seems likely that the leuco dyes are well dispersed in print pastes. It must be observed that these experiments do not show that the dye is molecularly dispersed, since a solution of a highly aggregated dye would still be clear visually.

Nevertheless, even though the dyes are soluble, it was necessary to determine whether combination between dye and the gum thickeners could occur, thereby causing dye to remain in the paste instead of being transferred to the fibre. This possibility

was examined for ten of the dyes by dyeing Bemberg (cuprammonium) rayon in the presence and in the absence of the gum thickeners. There was little difference between the results. Thus it seems that these factors do not influence to any great extent the ultimate colour yield.

As regards the diffusion processes, it was suggested in the previous paper² that the scanty data available indicated that diffusion of the dye into the fibre did not control the printing efficiency of the dye. This has been confirmed in the present work by measurements of diffusion coefficients of the dyes into Cellophane sheet at 95°C. under dyeing conditions. In all cases the diffusion was found to be extremely rapid. With regard to transfer of dye through the paste, no experiments have been made, although it seems that this may be of some importance⁷.

The affinities of the dyes were measured under dyeing conditions in a 1000:1 liquor containing 6.4 g. caustic soda, 14 g. sodium hydrosulphite, and 20 g. sodium chloride per litre. The amounts of dye on the fibre and in the dyebath were estimated colorimetrically, and the affinities calculated by the method described by Fowler, Michie, and Vickerstaff⁸. In Fig. 9 the results are compared

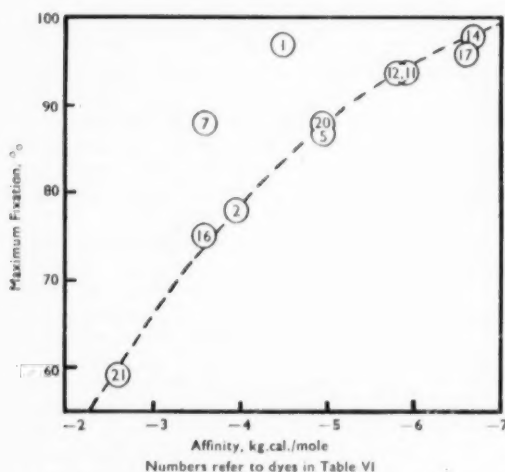


Fig. 9—Relation between the Affinity of Vat Dyes and the Percentage Maximum Fixation

with the "maximum fixation" of the dyes⁶, which are numbered according to Table VI. The results show that a dye with a high affinity has a high maximum fixation, and confirm the view that transfer of dyes from paste to fibre depends on at least one of their dyeing properties, namely their affinities.

DISCUSSION AND CONCLUSIONS

In the foregoing experiments, it has been tacitly assumed that the reduction and the fixation of the dye may be considered separately. This is not strictly true, since both processes occur simultaneously. As soon as the dye begins to be reduced, it can be absorbed by the fibre, and this continual

removal of dye from the paste will render more difficult any accurate correlation between printing and any one of the dye properties measured here. For example, with a reducing system which yields a reduction potential of -780 mv. it is possible to reduce Caledon Violet R to the extent of 50% (curve II, Fig. 1). Since this potential is governed by the concentration of reduced dye according to equation (ii), removal of the leuco compound by the fibre will promote further dye reduction, perhaps leading ultimately to complete adsorption. It is not, therefore, necessary in such circumstances to reach a leuco potential of -817 mv. in order to produce complete reduction. This particular example is extreme in that the behaviour of the dye is far from ideal. For a dye such as Caledon Yellow GN (Curve I), which behaves more normally, the amount reduced at potentials less negative than the leuco potential is so small that transfer to the fibre from the extremely dilute leuco solution will occur at a negligible rate. In such a case it is necessary to have a reducing agent with a potential more negative than the leuco potential before transfer can occur at a reasonable speed. For these reasons, however, and the variation of the leuco potential with concentration (equation (ii)), correlation between the leuco potentials and the Formosul sensitivity can never be perfect.

Again, the correlation between affinity and amount of dye fixed depends on sufficient time being allowed for dye transfer to take place. If the diffusion of the dye through the paste itself is slow, as a comparison of the rates of reduction with those of fixation would suggest, exceptions will again occur. Nevertheless, these effects must be of relatively minor importance in most cases, for the results show that there is in fact quite good correlation between affinity and percentage dye fixation. The overall picture of the printing process which may be developed from the present work is therefore as follows—

For high fixation the dye must be reduced rapidly and completely. In other words, the concentration of reducing agent required to bring about reduction varies from dye to dye, being low for dyes with small negative leuco potentials and *vice versa*. A most important factor in this connection is that the initial value of the potential of the paste, which gives a measure of its reducing strength, must be maintained for a sufficiently long time to effect reduction. It is therefore necessary to take into account the rate of decomposition of the Formosul under steaming conditions, as this determines how long the potential and therefore the reducing strength of the paste is maintained. When the paste contains sufficient agent to reduce the dye, the rate of reduction becomes the next factor determining printing behaviour, the time required for transfer of dye to the fibre depending to some extent on how quickly the leuco dye is formed.

When the dye is reduced, adsorption on the fibre is determined by the normal dyeing properties. The leuco dyes are in the fully ionised form and are apparently soluble in the print pastes. Diffusion into the cellulose itself is rapid, although diffusion through the paste may be slow. The amount of dye

transferred to the fibre appears to be connected with its affinity, presumably because equilibrium conditions between the print paste and the fibre surface are attained after about 10 min. steaming time.

* * *

The authors wish to thank Miss B. Taylor and Mr. A. Zeligman for assistance in the practical work.

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Addendum

When the work reported here was envisaged, it was decided in the first instance to measure "leuco potentials" under standard conditions of temperature, caustic soda concentration, and in particular dye concentration (5×10^{-4} M.). However, it became quite evident that in general the dyes did not behave ideally, i.e. did not obey equation (ii), and showed values of the reversibility α which differed markedly from unity. These different values of α mean, from the practical point of view, that for any particular alteration in concentration of dye, the extent to which the potentials change varies according to the dye. For example, the potential of Caledon Brilliant Violet R with a value of $\alpha = 0.19$ will change more than that of Caledon Brilliant Purple 4R with $\alpha = 1.00$ and a dye concentration must be reached when the former has a more negative potential than the latter and hence would be more difficult to reduce.

It follows therefore that the potentials given in Table III are a first approximation to the reduction behaviour of the dyes, but that a better comparison would be between the leuco potentials measured at the same concentrations as those used in practice. With this in mind leuco potentials have been determined at the same concentrations as were employed by Michie and Thornton in their experiments to determine the Formosul sensitivities. The technique already described was employed with the modification that only the first part of the titration curve was determined.

In one or two cases precipitation of the leuco form of the dye occurred at these high concentrations. This was overcome by the addition of a small quantity of glycerol. The results are given in Table VIII.

The potentials are more negative than those in Table III and the order has been slightly modified. For example, Caledon Brilliant Violet R now has a

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TABLE VIII
Leuco Potentials of Vat Dyes at
Printing Concentrations

Dye	Leuco Potential (mv.)	Critical Formosul Concn. in Potash Print Paste (%)
10% Caledon Printing Yellow 5GS	-979	5
10% Caledon Brilliant Violet RS Paste	-958	5
10% Caledon Printing Brown 4RS	-935	5
7.5% Caledon Printing Red 3B 200	-926	6
15% Caledon Printing Brown RS	-923	7
5% Caledon Printing Purple 4RS	-901	2
5% Caledon Printing Jade Green XNS	-877	2
15% Caledon Printing Blue GCPS	-865	1
10% Caledon Printing Orange 6RS	-845	1
10% Durindone Printing Brown GS	-817	2
5% Durindone Printing Blue 4BRS	-792	0
10% Caledon Printing Red BNS	-760	0
10% Caledon Printing Yellow GNS	-753	0
10% Durindone Printing Scarlet YS	~-734	2

potential of -958 mv. compared with Caledon Brilliant Purple 4R at -901 mv. (cf. potentials of -817 mv. and -835 mv. respectively given in Table III). Comparison with the Formosul sensitivity is now extremely good, there being no exceptions to the statement that the leuco potential determines this property.

(Received November 1953)

Discussion

MR. F. J. E. BANNING: What are the authors' views on the relation between the time to reach 50% of maximum reduction and the time to reach maximum oxidation? I was thinking about this when overlooking Table VI and comparing dye-stuff No. 12 and No. 21, No. 12 needing 45 sec. whereas No. 21 needs 100 sec. to reach 50% of maximum reduction, and I experienced that No. 12 oxidises quickly whereas No. 21 needs a very long time to get maximum oxidation. By knowing the

relation it might be possible to foretell by studying the time to reach 50% of maximum reduction whether the time to reach maximum oxidation would be long or short.

Connected with this relation it is also very interesting to notice No. 12 needs 900 sec. to reach 50% of maximum fixation whereas No. 21 needs only 600 sec.

MR. MARSHALL: It has been found in previous work² that the reduction rate depends not only on

the chemical constitution of the dye but also on the physical form of the crystals, and this latter effect is of considerable importance; thus the reduction rate depends on the rate at which a solid phase comes into solution whereas the rate of oxidation depends solely on the rate at which the soluble leuco form is oxidised and therefore does not depend on the final nature of the oxidised dye which may be greatly modified by subsequent treatment. Thus until more is known of the nature of the reduction and oxidation reactions one cannot speculate as to the relation between them.

Mr. D. A. DERRETT-SMITH: It is stated that the reduction potential of a vat dye is a measure of the intrinsic ability of the dye to become reduced. What is the relation between the reduction potential and the ease of vatting?

Dr. PETERS: Ease of vatting takes into consideration two aspects, viz. the rate at which the dye reduces, and whether it is possible to reduce the dye completely. In theory, the question of the completeness of reduction is governed by the reduction potentials, which bear no relation to the rate at which the dyes are reduced. In practice however, if the dye has a reduction potential near that of the reducing agent which is to reduce it, the reduction rate will be slow. The converse is not true, as is shown by the slow rate of reduction of some of the Durindone dyes.

Mr. T. W. RUWNOF: (1) The reduction process is rather complicated. If hydrogen ions are present or are liberated, the hydrogen-ion concentration, i.e. the pH, will be of importance. Would it not be useful to measure pH and redox-potential at the same time?

(2) When using the leuco potential technique of Fordemwalt, did you get any trouble with supersaturation?

(3) Has particle size and particularly agglomeration of particles in printing pastes any influence on the rate of reduction?

Dr. PETERS: (1) Redox potentials are pH-sensitive only when there is a substantial quantity of the undissociated quinol form of the dye. In the experiments described here the alkalinity is sufficiently high for the reduced dye to be completely dissociated.

(2) Supersaturation of the solution with the oxidised form of the dyes during titrations did occur with one or two of the dyes but was allowed for in the estimation of leuco potentials by extrapolation of the titration curve to the point at which the oxidised form was just precipitated. Since the titration curve was nearly horizontal to the abscissa this caused little or no error.

(3) Some work on the effects of particle size on rates of reduction has been reported previously², and it has been shown to have only a comparatively small effect. It seems unlikely, therefore, that if the dye particles agglomerate the rate would be much affected.

Mr. W. FURNESS: In Table III, about one-quarter of the results for α , the reversibility of the reaction, exceed unity. As α cannot really exceed

unity, do these results signify that the value chosen for α in equations (i), (ii) is slightly low, and, if so, would this mean that slight over-reduction of some dyes had occurred?

Mr. MARSHALL: While α exceeds unity for certain of the dyes, it exceeds it by only a small amount, and we consider that, in view of the well known experimental difficulties involved in electrometric work of this nature, the true value is unity. So far as the suggestion that a value in excess of one indicates slight over-reduction is concerned, we do not think that this is so because, in addition to the above reasons, the two dyes which this particularly concerns, namely Caledon Red BN and Caledon Yellow GN with values of 1.1 and 1.2 respectively, are both considered to be dyes of considerable stability to over-reduction.

Mr. H. A. TURNER: I am interested in the laboratory steamer used in this work (Fig. 8), for it appears to be a useful development of a simpler one that we have employed. I can appreciate that, in the present work, where an optical measurement is made with the printing system in the steam, condensation on the wall either of jacket or steaming chamber must be avoided. Nevertheless, we have found that dye transfer is sensitive to very small degrees of superheat in the steam. We have always taken condensation on the walls of the jacket to be a safeguard against unsaturation. With the supplementary electric heaters in action, what precautions are taken to ensure that the steam is fully saturated?

Mr. MARSHALL: Mr. Turner appreciates many of the difficulties which we have encountered in this type of study and in particular one of these was to avoid excessive moisture in the steam rather than excessive dryness and in fact the potash formosul paste very readily took up excess moisture to such an extent that it formed streaks down the slide. Our procedure was thus as follows—

The outside electric heater was adjusted to such a value that the inside temperature of the steamer was maintained at a value of between 90 and 100°C. without steam. In this way heat losses were almost entirely counterbalanced by the electrical heating. Steam was then passed through a heated copper coil before going into the steamer, the temperature of the coil being adjusted so that streaking of the paste on the slides was just avoided. That the steam was sufficiently wet was clearly indicated by the dampness of the paste on the slide in the steamer and immediately on being withdrawn from the steamer.

Mr. TURNER*: I am very much intrigued by the use of chopped material to represent the fibre phase, and feel that this expedient might suggest directions in which we could modify our own experiments when we come to study dye transfer to actual fibres, a thing we would like to do. At present, however, I do not see how the thickener could be separated from the fibres, at the end of the steaming period, without a risk of upsetting the dye distribution. Have the authors any suggestions?

Mr. MARSHALL*: While we agree with Mr. Turner

* Communicated

that this type of technique would be very useful for studying the adsorption of vat dyes by fibres, there would be considerable difficulty in studying the equilibrium of water soluble dyes. However we might make the following suggestion, since the

paste is relatively fluid at high temperature it might be possible rapidly to wash off the paste and fibre mixture into a rapid filtering sintered glass filter using ice cold water saturated with salt but even this would be not altogether satisfactory.

An Investigation of the Chemical Reactions Involved in the Use of Sodium Formaldehyde-sulphoxylate in Textile Printing

R. J. HANNAY and W. FURNESS

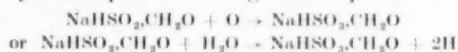
In discharge printing with sodium formaldehyde-sulphoxylate, reduction of the dye is accompanied by oxidation of the formaldehyde-sulphoxylate to formaldehyde-bisulphite. Although some preliminary decomposition has been noted during drying of the cloth immediately after printing, the main object of this investigation has been to determine the extent, and to trace the products, of decomposition of the formaldehyde-sulphoxylate during the steaming of a printed and dried filament viscose-rayon crêpe.

Methods of analysis are described. Their use has shown that the extent of decomposition of the formaldehyde-sulphoxylate on steaming depends very much on other constituents of the printing paste. In particular, the influence of added sodium carbonate and sodium sulphite in pastes made up with British gum and gum tragacanth has been traced, and the effect of leaving printed goods overnight in warm storage before steaming has also been investigated.

Fluidity tests showed that no appreciable tendering of the crêpe occurred under any of the conditions imposed in this investigation.

The use of sodium formaldehyde-sulphoxylate as a discharging agent in textile printing was established as long ago as 1905, the product having been discovered by the Badische Anilin- und Soda-Fabrik in the previous year. It was quickly recognised that the use of this reducing agent offered many advantages over the earlier methods employed, and following its first use in 1905 it gradually established itself, until it is now universally used and is the most important reducing agent employed in textile printing.

During the intervening period many investigations have been carried out relating to the use and manufacture of the sulphoxylates, and the results have been published in the technical press; but it is rather significant that very little has been published relating to the chemical reactions and degradation products which are produced when the sulphoxylates are used in printing, and it is still true to say that comparatively little is known about this aspect of the process and its effect on the resulting prints. It may be that one reason for this lack of information has been the absence, until quite recently, of suitable analytical techniques which would distinguish between the various oxidation products formed and would allow their quantitative estimation in presence of one another. But, whatever the reason, it is certain that the generally accepted view, that the reducing action of sodium formaldehyde-sulphoxylate results in its oxidation to sodium formaldehyde-bisulphite according to the equation—



whilst being true in substance, is a very much over-simplified explanation of what actually happens in practice. The work described in this paper is an attempt to provide some reliable information on the manner in which sodium formaldehyde-sulphoxylate decomposes when used for discharge printing under works conditions and on the effect of varying conditions on the resulting prints.

A series of experiments was devised in which sodium formaldehyde-sulphoxylate was used in different printing pastes for producing a white discharge effect on a filament viscose-rayon crêpe fabric previously dyed navy blue with Diazamine Blue BR coupled with β -naphthol. A detailed analysis of the various printing pastes was followed by an analysis of the products contained in the

printed portions of the fabric—(X) after printing and drying only; (Y) after printing, drying, and steaming on the same day; and (Z) after printing and drying followed by steaming only after a delay of 24 hr. storage in hot goods.

The choice of filament viscose-rayon crêpe fabric as substrate was made because of the knowledge that occasionally, under certain unknown conditions, a degradation of cellulose may occur during the processes involved in discharge printing with sulphoxylates. Any such action is emphasised when viscose rayon is used as substrate in comparison with cotton, and therefore it appeared advisable to use this fibre, which could be expected to throw into relief any reaction tending to produce degradation of cellulose. In addition to this, it is known that crêpe fabrics of this type are very popular materials for the production of discharge prints. Diazamine Blue BR was selected as the ground dye on account of the large amounts used for this purpose in the printing trade. Fluidity tests on both unprinted and printed portions of the fabric were made.

The printing pastes used in these trials were made up as shown in Table I.

TABLE I
Printing Pastes

A—BASIC RECIPES				
	No. 1	No. 2	No. 5	No. 6
Formosul, g. ...	20	20	20	20
Soda ash, g. ...	—	—	9	9
British gum paste, c.c.	80	—	80	—
Gum tragacanth paste, c.c.	—	60	—	60
Colour oil, c.c.	10	10	10	10
Water to make up to, c.c.	150	150	150	150

ADDITIONAL RECIPES

- B—Basic recipe + 1.5 g. sodium sulphite
($\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$)
- C—Basic recipe + 1 c.c. of 10% sodium sulphide soln. per 500 c.c. print paste
- D—Basic recipe + 1.5 g. sodium sulphite + 1 c.c. of 10% sodium sulphide soln. per 500 c.c. print paste.

The printing roller used was a $\frac{1}{2}$ -in. stripe equally spaced with 50% coverage and putting on the cloth approx. $1\frac{1}{4}$ gal. of print paste per 120 yd. \times 36 in. After being printed, the cloth was dried in the normal manner over steam-heated copper cylinders and steamed for 10 min. in a modern festoon-type steamer.

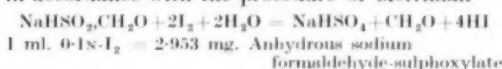
Analytical Procedure

The identification and the determination of the salts printed on to the crêpe and of their decomposition products were carried out by applying volumetric and polarographic methods to the aqueous extract of portions of the printed fents. As soon as possible after receipt of the processed cloth (see above), an area equal to 290 sq.cm. of the printed portion of the crêpe (i.e. a total length of 200 cm. of the printed stripe \times its width of 1.45 cm.) was sampled and cut into pieces of approximate area 1 sq.cm. These were stirred for 1 hr. with 150 ml. of water at 15–18°C. in a flask, closed to the atmosphere, through which a stream of nitrogen was passed continuously to prevent the accidental oxidation of any constituent. The solution was then separated by filtration through a Hirsch funnel, the pieces of crêpe were pressed on the filter and washed with cold water, and the solution and the washings were diluted to 250 ml. Preliminary tests had confirmed that by this procedure virtually complete dissolution of all the soluble salts was assured whether British gum or gum tragacanth was included in the printing paste.

The printing pastes themselves were prepared for analysis by dissolving 8 g. in water and diluting to 500 ml.

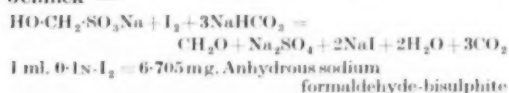
1. DETERMINATION OF SODIUM FORMALDEHYDE-SULPHOXYLATE

A 50-ml. aliquot of the aqueous extract was added to 2 ml. of 36% formaldehyde solution, and the resulting solution was acidified slightly by dropwise addition of acetic acid. It was titrated with decinormal iodine, starch being used as indicator, in accordance with the procedure of Merriman¹—



2. DETERMINATION OF SODIUM FORMALDEHYDE-BISULPHITE

The solution remaining after titration with iodine in procedure (1) is neutralised with solid sodium bicarbonate, and 3 g. sodium bicarbonate added in excess. This solution is warmed to 40–45°C., and titrated at this temperature with decinormal iodine. The reaction is slow, especially towards the end of the titration, but, when it has been reached, the equivalence point is indicated distinctly by the starch. This procedure is based upon the work of Jellinek²—



If free sodium sulphite is present in the aqueous extract, it is converted to sodium formaldehyde-bisulphite in procedure (1) and titrated in procedure (2). Under these conditions—



When the concentration of free sodium sulphite has been determined polarographically in accordance with procedure (3) below, the appropriate deduction must be made in calculating the sodium formaldehyde-bisulphite.

3. DETERMINATION OF SODIUM SULPHITE

A 25-ml. aliquot of the aqueous extract is transferred to a 50-ml. graduated flask and diluted to 50 ml. with the buffer solution—

- 0.76 M. Potassium dihydrogen phosphate
- 0.04 M. Disodium hydrogen phosphate
- 0.002% Quinoline.

A polarogram of the solution at 25.0°C. is recorded between –0.2 v. and –1.0 v. against the saturated calomel electrode (S.C.E.) so as to show the cathodic reduction of the bisulphite ion, whose half-wave potential lies between –0.63 v. and –0.70 v. (S.C.E.) at the concentrations under investigation. The limiting diffusion current at –0.85 v. (S.C.E.) is proportional to the concentration of bisulphite, and—

$$\frac{I_d}{C_m^{1/2}t} = 2.20$$

I_d = Limiting diffusion current, expressed as the average current in μA . flowing during the life-time of a single mercury drop

C = Concentration of total free sulphite, millimoles per litre of the buffered solution

m = Rate of flow of mercury through the capillary, mg./sec.

t = Drop time, sec.

4. DETERMINATION OF SODIUM THIOSULPHATE, SULPHIDE, AND TRITHIONATE

These were determined polarographically by applying the methods previously described³ for the determination of these salts in commercial hydro-sulphites. For the present application of these methods, the determination of thiosulphate required a small addition of formaldehyde to the potassium nitrate supporting electrolyte to prevent interference on the polarogram from sulphite, but the determination of sulphide and trithionate was possible without any addition of formaldehyde to their respective supporting electrolytes.

Results of Analysis and their Significance

The printing pastes were examined only for the constituents mentioned in Table II. Sulphate, though not determined exactly, was present in all the pastes to the extent of about 0.01–0.03%, but no other sulphur compounds were found. The pH

TABLE II
Analysis of Discharge Printing Pastes

Sample	Percentage (weight/weight) of*—					pH of Aq. Soln.
	$\text{NaHSO}_2\text{CH}_2\text{O}$	$\text{HO-CH}_2\text{SO}_3\text{Na}$	Na_2SO_3	$\text{Na}_2\text{S}_2\text{O}_4$	Na_2S	
1A	7.26	1.84	<0.02	0.10	<0.02	3.78
5A	7.60	1.25	<0.02	<0.05	<0.02	10.40
2A	7.98	1.55	<0.02	0.05	<0.02	5.44
6A	9.31	0.66	0.32	<0.05	<0.02	10.22
1B	7.60	1.59	0.63	0.12	~0.02	7.56
5B	7.02	1.32	0.72	<0.05	<0.02	10.32
2B	8.98	1.53	0.60	<0.05	<0.02	7.15
6B	9.10	1.35	0.79	<0.05	<0.02	10.38
2C	8.25	1.31	<0.02	<0.05	~0.02	6.70
2D	9.55	1.45	0.66	<0.05	~0.02	7.62
6C	9.05	1.46	0.22	<0.05	~0.02	10.40
6D	8.99	1.21	0.76	<0.05	~0.02	10.40

*The methods of analysis employed would have detected sodium thiosulphate if this had been present at a concentration of 0.05%. None was found in any of the above samples.

TABLE III
Analysis of Aqueous Extract of Crêpe, pH of Extract, and Fluidity of Bleached Crêpe

Printing Paste*	Fent	Salts (mg.) extracted from 1 sq. dm. of printed crêpe†—					Sulphur (total equiv., mg.)	Formo- sul decom- posed during Steam- ing (%)	pH of Aq. Extract	Fluid- ity‡ (poise ⁻¹)
		NaHSO ₃ CH ₂ O	HOCH ₂ SO ₃ Na	Na ₂ SO ₃	Na ₂ S ₂ O ₃	Na ₂ S ₂ O ₄				
1A British gum ...	X	100.9	35.6	<0.5	<1	4.8	37.8	—	6.40	—
	Y	55.0	69.5	<0.5	3.2	1.0	33.2	46	6.82	9.9
	Z	53.0	73.8	<0.5	2.6	<1	33.2	47	6.90	10.4
5A British gum + Na ₂ CO ₃ ...	X	100.1	22.0	0.9	1.3	5.0	35.2	—	10.28	—
	Y	9.9	62.9	13.0	<0.5	2.0	21.8	90	10.37	8.6
	Z	8.6	63.5	13.0	<0.5	1.0	21.2	91	10.38	8.9
2A Gum tragacanth ...	X	110.0	18.9	<0.5	<1	1.2	34.8	—	7.40	—
	Y	35.5	75.8	<0.5	1.9	<1	28.5	68	6.84	11.0
	Z	38.6	74.9	<0.5	1.9	<1	29.2	65	7.04	9.8
6A Gum tragacanth + Na ₂ CO ₃ ...	X	109.9	28.4	0.9	<1	<1	36.8	—	10.25	—
	Y	27.4	74.6	9.6	<0.5	<1	27.6	75	10.20	9.0
	Z	36.5	54.2	19.6	0.6	<1	28.1	67	10.55	8.7
1B British gum + Na ₂ SO ₃ ...	X	97.1	41.6	2.6	1.0	4.2	39.2	—	8.00	—
	Y	54.8	77.5	3.0	3.2	<1	35.5	44	7.20	9.9
	Z	55.3	73.3	2.6	2.6	<1	34.3	43	7.22	8.9
5B British gum + Na ₂ SO ₃ + Na ₂ CO ₃ ...	X	86.2	35.5	5.6	1.6	6.0	36.4	—	10.24	—
	Y	8.9	61.9	13.9	0.6	<1	20.9	90	10.40	8.1
	Z	8.6	69.5	14.8	<0.5	1.2	23.2	90	10.48	10.4
2B Gum tragacanth + Na ₂ SO ₃ ...	X	122.2	30.9	5.6	1.6	4.8	44.6	—	8.41	—
	Y	56.6	82.3	3.9	2.6	<1	37.2	54	7.28	10.9
	Z	59.6	77.2	4.4	3.2	1.2	37.6	51	7.36	8.9
6B Gum tragacanth + Na ₂ SO ₃ + Na ₂ CO ₃ ...	X	105.6	33.2	5.6	1.0	5.1	40.4	—	10.40	—
	Y	21.6	79.3	18.7	1.3	<1	30.2	80	10.40	8.6
	Z	32.5	74.8	26.1	1.9	<1	34.1	69	10.42	10.9
2C Gum tragacanth + Na ₂ S ...	X	100.1	21.3	<0.5	<1	3.7	33.8	—	7.68	—
	Y	26.1	81.0	<0.5	1.3	1.5	27.6	74	6.54	10.1
	Z	40.1	70.3	<0.5	3.8	<1	29.2	60	7.00	11.2
2D Gum tragacanth + Na ₂ S + Na ₂ SO ₃ ...	X	105.8	17.1	6.7	<1	6.0	36.9	—	8.26	—
	Y	53.3	88.7	2.2	1.3	1.2	37.3	50	7.89	9.9
	Z	62.0	89.5	5.2	2.6	0.9	41.0	41	7.46	10.0
6C Gum tragacanth + Na ₂ S + Na ₂ CO ₃ ...	X	98.6	25.8	<0.5	<1	2.5	34.0	—	10.30	—
	Y	21.1	68.0	8.7	1.9	1.0	25.4	79	10.35	10.1
	Z	30.2	50.3	16.1	1.9	<1	25.1	69	10.35	11.0
6D Gum tragacanth + Na ₂ S + Na ₂ SO ₃ + Na ₂ CO ₃ ...	X	105.6	33.7	5.2	<1	4.2	39.7	—	10.38	—
	Y	22.8	78.1	18.7	<0.5	1.2	30.2	78	10.30	9.5
	Z	39.3	63.4	21.7	1.9	<0.5	32.2	63	10.50	9.7

*Components in addition to Formosul and colour oil.

†The methods of analysis employed would have detected sodium sulphide if this had been present at a concentration of 0.2 mg. of Na₂S per square decimetre of print. None was found in any of the above samples.

‡Average fluidity of the dyed unprinted crêpe fabric 8.1 poise⁻¹.

of their aqueous solutions was determined when 8 g. was diluted to 500 ml.

Table III reports the results obtained by analysis of the aqueous extracts of printed portions of all the fents. These are grouped so as to show for each composition of printing paste the weights of sodium formaldehyde-sulphoxylate and of various other sulphur compounds found on unit area of the printed and dried fents (series X), on the fents that had been steamed the same day (series Y), and on those steamed after a delay of 24 hr. (series Z).

A comparison between the ratios of sodium formaldehyde-bisulphite to sodium formaldehyde-sulphoxylate for the original printing pastes (Table II) and for the corresponding printed and dried fents (series X—Table III) shows clearly that some decomposition of the sulphoxylate must occur while the freshly printed crêpe is being passed over the drying rolls. The data are not sufficiently complete to permit an exact estimate of the extent of decomposition at this stage, but in the worst case

(6D) approx. 14% of the sulphoxylate that was applied to the crêpe suffered decomposition during drying, and in the least serious case (2D) approx. 59% decomposed. As far as can be ascertained, there is no correlation between the extent of decomposition during drying and the composition of the printing paste.

The percentage of sodium formaldehyde-sulphoxylate that decomposes during steaming can, however, be calculated with much greater accuracy if it is assumed firstly that the discharge paste was printed uniformly on to the whole length of crêpe from which fents X, Y, and Z were cut, and secondly that any decomposition on drying occurred uniformly over this entire length. The procedure during printing and drying was such that these are reasonable assumptions.

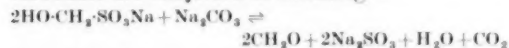
(1) We consider first the differences between series Y and Z for individual printing-paste compositions. When British gum is used, a delay up to twenty-four hours between the drying of the print

and steaming causes no really significant change in the extent of decomposition of the Formosul. On the other hand, when gum tragacanth has been incorporated instead, the extent of decomposition of the Formosul during steaming is always appreciably lower if the printed and dried crêpe has first been allowed to lie in hot goods for a whole day. This may be evidence that on aging a physical change occurs in the surface properties of the dried printing paste which causes it to become more impervious when finally submitted to steaming. The analyses do not disclose any chemical changes in the constituents printed on to the crêpe that could be attributed to warm storage.

(2) A principal oxidation product of sodium formaldehyde-sulphoxylate is sodium formaldehyde-bisulphite. It can be anticipated that removal of the latter from the system would promote the decomposition of the sulphoxylate. The dissociation of sodium formaldehyde-bisulphite in aqueous solution is a reversible reaction, the equilibrium position depending on the hydrogen ion concentration—



Thus, when printing pastes containing sodium carbonate are subjected to steaming—



some formaldehyde and carbon dioxide will be removed, and free sulphite will be found among the decomposition products.

Consideration of the figures tabulated for the percentage of Formosul decomposed on steaming, i.e. 5A-1A, 5B-1B, 6A-2A, 6B-2B, 6C-2C, 6D-2D, shows that the introduction of sodium carbonate always promotes the decomposition of Formosul during steaming of the printed crêpe. This effect is most noticeable when British gum has been used in preparing the discharge paste. No matter whether sodium sulphite has been included in the composition, the sodium carbonate addition raises the extent of decomposition of Formosul during a 10-min. period of steaming from about 45 to 90%.

In the printing-paste compositions incorporating gum tragacanth this effect of sodium carbonate is not quite so marked. For example, in the absence of sodium sulphite a comparison of 6AY with 2AY shows that the addition of sodium carbonate has increased the extent of decomposition by only 7%, whilst in the presence of a trace of sulphide (6CY-2CY) the effect was similarly 5%. However, in pastes based on gum tragacanth which include also sodium sulphite, the effect of sodium carbonate is to promote substantially the extent of decomposition of the Formosul. This is illustrated by a comparison between 6BY and 2BY, where decomposition increased from 54 to 80%; similarly, in the presence of a trace of sulphide (6DY-2DY) the increase was from 50 to 78%.

Wherever sodium carbonate has been incorporated in a discharge printing-paste composition, very substantial quantities of sodium sulphite have been found among the decomposition products. This is in accordance with the view, expressed above, that in the presence of alkali dissociation of sodium

formaldehyde-bisulphite must occur during steaming, with consequent volatilisation of formaldehyde. When the printed and steamed crêpe passes out of the steaming cabinet, the free sulphite will tend to combine with the oxygen of the atmosphere, and this tendency will be greater wherever alkali is also present. Indeed, sulphate was always detected among the decomposition products extracted from the steamed fents, and though the quantities were not determined, it was obvious that fents printed with the strongly alkaline discharge pastes were those upon which most sulphate was formed. Leaving out of consideration case 2D, it will be noted that the total weight of sulphur, equivalent to the salts $\text{NaHSO}_2\text{CH}_2\text{O}$, $\text{HO-CH}_2\text{SO}_3\text{Na}$, Na_2SO_3 , $\text{Na}_2\text{S}_2\text{O}_3$, $\text{Na}_2\text{S}_3\text{O}_6$, and Na_2S found on each square decimetre of printed crêpe, is always smaller after steaming (series Y, Z) than before steaming (series X). These differences are not really discrepancies, because Table III takes no account of the quantity of sulphate formed during or immediately after steaming; the figures are, in fact, consistent with the observation that the more sulphate is formed on those fents printed with strongly alkaline discharge pastes.

(3) The experimental results reported in Table III show that the addition of sodium sulphite may hinder the decomposition of sodium formaldehyde-sulphoxylate during steaming. This appears to be the case when, at the same time, the paste is virtually neutral in reaction and is based on gum tragacanth.

For example, the compositions 2A and 2B are both practically neutral and differ only by the incorporation of sodium sulphite into 2B. The percentages of sodium formaldehyde-sulphoxylate decomposed during steaming of the fents 2AY and 2BY are 68 and 54 respectively. Similarly, the compositions 2C and 2D differ only in the addition of sodium sulphite to 2D; for this pair, the figures for the decomposition of the sulphoxylate are 74 and 50%.

However, when sodium carbonate also is incorporated into discharge-printing compositions based on gum tragacanth, this effect of sodium sulphite is much less pronounced or even slightly reversed. This is illustrated by a comparison of the results for 6AY and 6BY, 6AZ and 6BZ, 6CY and 6DY, and 6CZ and 6DZ.

In view of these effects, it is surprising to note from Table III that, when British gum is used instead of gum tragacanth, the presence of sodium sulphite seems to have no really significant effect on the extent of decomposition of Formosul during steaming. Furthermore, in compositions based on British gum that include sodium carbonate, the presence or absence of sodium sulphite is immaterial.

(4) The drying of discharge pastes of all the compositions considered here is attended by the formation of small amounts of sodium trithionate. Table III shows that the trithionate is usually decomposed completely during steaming. In ordinary alkaline aqueous solutions, sulphide is the principal product resulting from the reduction of trithionate. Although sensitive tests were applied,

the presence of sulphide could not be confirmed on any of the steamed fabrics, and the route by which trithionate decomposes under these conditions requires further investigation.

(MS. received 13th July 1953)

Second Series of Trials

As no evidence of appreciable tendering of the viscose was obtained under any of the conditions imposed during the first set of trials, a second series was devised altering certain of the conditions. It is important to keep clearly in mind the operating conditions of the first series, namely—

1. The atmospheric conditions were dry and fine with a low air humidity.
2. The steaming conditions were such that the steam used was relatively dry, as the trials were run through the steamer during a long run of vat print styles.
3. After steaming the trial prints were quite dry and were kept in a sealed container until the completion of the analytical work.

It is obvious from the analytical results that under such conditions the Formosul on the printed fabric is relatively stable, as little loss in Formosul content was shown even after keeping for over a week. In the second series of trials the operating conditions were quite different, as follows—

1. The atmospheric conditions were humid, the day on which they were carried out being very wet.
2. The steaming conditions were adjusted by running damped cloth into the steamer prior to putting the trials through.
3. In the case of six of the trials a deliberate addition of 5% glycerine was made to the print pastes as a hygroscopic agent.
4. The printed and the printed and steamed fabrics were allowed to stand 24 hours exposed to atmospheric conditions before being placed in the sealed container.

It will be seen from the following account that under these conditions the results are quite different from those obtained in the original trials.

The printing pastes used in this second series were made up as shown in Table IV.

	7	8	9	10	11	12	13	14
Formosul ...	20 g.	20 g.	20 g.	20 g.	20 g.	20 g.	20 g.	20 g.
Gum tragacanth ...	60 c.c.	60 c.c.	60 c.c.	60 c.c.	60 c.c.	60 c.c.	60 c.c.	60 c.c.
Colour oil ...	10 c.c.	10 c.c.	10 c.c.	10 c.c.	10 c.c.	10 c.c.	10 c.c.	10 c.c.
Soda ash ...	—	—	—	—	9 g.	9 g.	9 g.	9 g.
Glycerol (80%) ...	—	7.5 c.c.	7.5 c.c.	7.5 c.c.	—	7.5 c.c.	7.5 c.c.	7.5 c.c.
Sodium sulphide ...	—	—	0.75 g.	—	—	—	0.75 g.	—
Titanium oxide ...	—	—	—	15 gr.	—	—	—	15 g.
Water to ...	150 c.c.	150 c.c.	150 c.c.	150 c.c.	150 c.c.	150 c.c.	150 c.c.	150 c.c.

The printing roller used was the same $\frac{1}{2}$ in. stripe roller used in the first series and the fabric was again a filament viscose-rayon crêpe previously dyed navy blue with Diazamine Blue BR coupled with β -naphthol.

Results of Analysis and their Significance

TABLE V
Analysis of Discharge Printing Pastes prepared on 31st August 1953

Sample	Percentage (weight/weight) of—					pH of Aq. Soln.
	NaHSO ₂ CH ₂ O	HO-CH ₂ SO ₃ Na	Na ₂ SO ₃	Na ₂ S ₂ O ₃	Na ₂ S ₂ O ₄	Na ₂ S
7	8.78	1.69	<0.05	<0.05	<0.05	0.05 5.00
8	8.40	1.94	<0.05	<0.05	<0.05	0.05 4.90
9	8.73	2.11	<0.05	0.25	<0.05	0.16 7.62
10	8.32	2.16	<0.05	<0.05	<0.05	<0.05 6.87
11	8.56	1.18	<0.05	<0.05	<0.05	<0.05 10.12
12	8.35	1.23	<0.05	<0.05	<0.05	<0.05 10.25
13	8.65	2.11	0.06	0.35	<0.05	0.18 10.38
14	8.15	1.69	0.06	<0.05	<0.05	<0.05 10.23

The main features of interest in this table are—

(a) The presence of between 8 and 9% of sodium formaldehyde-sulphoxylate confirms that the pastes were not deficient in this constituent.

(b) The presence of 0.16 and 0.18% of Na₂S in samples 9 and 13 corresponds to 0.50 and 0.56% of added Na₂S.9H₂O to the print pastes.

(c) In the pastes to which sulphide was added, thiosulphate has also been detected. This can only have arisen as a result of slight decomposition of the sodium formaldehyde-sulphoxylate and is presumed to have been induced by the sulphide.

(d) The pH values confirm the presence of sodium carbonate in samples 11, 12, 13 and 14.

The analyses of the the printing pastes were carried out on the 4th and 7th September. On the 8th, 9th, 10th and 11th September the analyses of aqueous extracts of the printed fabrics were carried out, the results of which are shown in Table VI.

It was noticed that by the 4th September the printed but unsteamed samples 7X, 8X, 9X and 10X were showing a discharge effect of the navy blue ground colour. No such effect was observed, however, on those samples printed with the alkaline pastes even after a period of 18 days after printing.

Table VI shows that nearly all the sodium formaldehyde-sulphoxylate on the printed fabric had decomposed during storage for seven days in a sealed container at room temperature (18°C.). This decomposition was just as extensive on those samples printed with alkaline pastes as on those printed with slightly acid or substantially neutral pastes, the latter having developed slight acidity during the storage period.

Throughout both series of trials the principal decomposition product of sodium formaldehyde-sulphoxylate has proved to be sodium formaldehyde-bisulphite, so that oxidation either by the absorption of molecular oxygen or in other ways

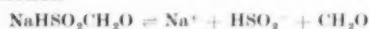
TABLE VI
Analysis of Aqueous Extract of Crêpe, pH of Extract and Fluidity of Bleached Crêpe

Printing Paste	Fent	Salts (mg.) extracted from 1 sq. dm. of printed crêpe*					pH of Aq. Extract	Fluidity (poise ⁻¹)†	
		NaHSO ₂ ·CH ₂ O	HO·CH ₂ ·SO ₃ Na	Na ₂ SO ₃	Na ₂ S ₂ O ₃	Na ₂ S ₂ O ₅		Crêpe washed after	
7 No other additions ...	X	3.0	81.6	< 0.5	< 1	3.6	3.62	3 hrs.	16.1
	Y	2.2	91.1	1.3	1.0	< 1	4.20	11 days	14.0
8 Glycerol ...	X	1.7	96.8	< 0.5	< 1	4.8	4.15	—	14.1
	Y	1.5	99.0	0.9	< 1	< 1	4.68	—	11.7
9 Glycerol + Sodium Sulphide	X	1.2	161.0	< 0.5	< 1	3.8	5.70	—	13.9
	Y	1.7	96.3	2.2	< 1	< 1	5.53	—	14.7
10 Glycerol + Titanium Dioxide	X	2.2	123.8	< 0.5	< 1	3.0	4.42	—	15.3
	Y	2.0	109.1	0.9	< 1	3.0	5.56	—	13.3
11 Sodium Carbonate ...	X	2.5	123.2	1.7	1.3	2.5	9.72	—	9.0
	Y	1.7	96.8	1.0	< 1	4.2	9.70	—	9.0
12 Sodium Carbonate + Glycerol	X	1.0	129.4	1.3	< 1	2.1	9.85	—	7.0
	Y	1.0	81.6	1.1	< 1	< 1	9.96	—	7.0
13 Sodium Carbonate + Glycerol + Sodium Sulphide	X	3.5	123.2	0.9	< 1	1.3	9.87	—	9.0
	Y	1.0	72.6	2.6	< 1	< 1	10.00	—	8.3
14 Sodium Carbonate + Glycerol + Titanium Dioxide	X	1.5	132.8	1.7	1.2	2.4	9.96	—	7.3
	Y	1.0	92.9	2.2	< 1	< 1	9.97	—	8.7

* Analyses made seven days after printing and steaming of crêpe. By this time in series 7, 8, 9, 10, partial bleaching of the unsteamed fents had occurred. The methods of analysis employed would have detected sodium sulphide if this had been present at a concentration of 0.2 milligram of Na₂S per square decimetre of print. None was found in any of the above samples.

† Average fluidity of the dyed unprinted crêpe fabric 7.6 poise⁻¹.

has occurred. We know from the first series that on fabric printed with a paste consisting only of Formosul, gum tragacanth and colour oil and then properly dried, the sodium formaldehyde-sulphoxylate shows no sign of decomposition that can be attributed to storage at room temperature if kept in a dry atmosphere. The only material difference between the second series of trials and the first is that steps were taken to ensure a good moisture regain in the printed fabric before storage, by manipulating the operating conditions and by incorporating some glycerine in a number of the pastes. We regard the results obtained as showing that under moist conditions of storing, no matter whether the paste is neutral or alkaline, the sodium formaldehyde-sulphoxylate transferred to the fabric during printing begins to decompose comparatively soon after printing. This decomposition, which can proceed at room temperature, is accompanied by partial discharge of the dyed ground only when the printing paste is neutral or slightly acidic in reaction. This difference can be shown in solutions, if to a solution of the dye Fast Red A (C.I. 176) e.g. a solution of Formosul is added and then the mixed solutions are slightly acidified with acetic acid, on warming to 35–40°C. the dye is quickly decolourised; on the other hand if the solution is made alkaline with sodium carbonate, no decolouring takes place under these conditions. It is known from work carried out in our own laboratories and from that of Bassett and Durrant⁴ that dissociation of the formaldehyde-sulphoxylate anion occurs much more rapidly in acidic solutions than in alkaline solutions. Hence, in the moist conditions that exist on those prints made under the conditions of the second series, the reaction

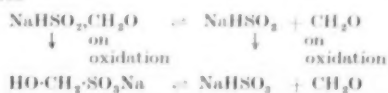


must proceed further to the right in the acidic than in the alkaline pastes. The formation of a powerful reducing agent such as the sulphoxylate ion is, in fact, demonstrated by the discharge

effect shown on the navy ground of the unsteamed samples 7X, 8X, 9X and 10X on storage at room temperature whereas on those samples 11X, 12X, 13X and 14X printed with alkaline pastes no such effect was produced.

Fluidity tests were carried out on samples of the printed fabric taken after washing off the prints (a) 3 hours after printing and (b) after storage for 11 days. The results which are presented in the columns on the extreme right of Table VI show that, whilst no significant tendering is shown in any of the prints which were washed off within 3 hours of printing, except perhaps in the case of 10Y in which the rise in fluidity is just approaching a significant value, all the prints produced with slightly acidic pastes are showing serious tendering after storage for 11 days, but those on which alkaline pastes were used are showing no signs of tendering even after this period of storage. This observation suggests that those conditions which are favourable to the formation of the acid sulphoxylate ion are those which also cause tendering of cellulose.

By oxidation of the acid sulphoxylate anion the bisulphite anion is formed, but in acidic media the bisulphite anion combines with formaldehyde to form the formaldehyde-bisulphite anion. We therefore postulate that, in slightly acidic printing pastes



the reactions proceed from NaHSO₂CH₂O to HO-CH₂SO₃Na by the clockwise route, and this would account for the fact that sodium formaldehyde-bisulphite is the principal decomposition product when using neutral or acidic printing pastes. On the other hand, when using alkaline printing pastes it would appear that oxidation of formaldehyde-sulphoxylate proceeds directly so as

to form formaldehyde-bisulphite, which afterwards dissociates to give free sulphite and formaldehyde, i.e. in an anti-clockwise direction as shown above. This view corresponds with the analytical results obtained, bearing in mind the oxidation of the free sulphite to sulphate which has always been found, particularly in the case of alkaline print pastes.

As in the first series of trials, Table VI again shows that sodium sulphide, which had been incorporated into printing pastes 9 and 13, is not to be found after these pastes have been applied to the fabric and then dried. The sulphide must therefore react with other constituents of the printing paste or with molecular oxygen.

The reaction $\text{H}_2\text{S} + \text{H}_2\text{SO}_3 \rightleftharpoons 2\text{S} + 2\text{H}_2\text{O}$ is discussed by Bassett and Durrant (*loc. cit.*). If this reaction were responsible for the disappearance of sulphide in the printed and dried fabrics, it should be possible to detect elementary sulphur. Tests on the sample 9X did in fact show that elementary sulphur had been deposited there.

Conclusion

The results of this investigation show that it is possible to cause degradation of cellulose and tendering of printed viscose fabrics by using a slightly acidic sodium formaldehyde-sulphoxylate discharge printing paste and storing the resulting steamed prints under moist conditions for a period of time, even at temperatures as low as 18°C. It is fairly obvious that a rise in the temperature of storage will accelerate the reactions and cut down the time required to produce this effect. This is indicated by the rapid decolorisation of Fast Red A in aqueous solutions which occurred in a matter of minutes at 40°C. The tendering effect is completely prevented when using alkaline discharge pastes.

Arising out of the results of this investigation a number of suggestions can be made to the printer for the prevention of tendering when printing sulphoxylate discharges on cellulosic materials.

1. The pH of the printing thickenings should be checked. It is perhaps not as widely recognised by colour shop men as it might be that a number of the thickenings regularly used are quite acid in aqueous solutions without the addition of any other acid substance. For example, a straight British Gum thickening frequently has a pH as low as 3.5, and even Gum Tragacanth can be as low as pH 4.0. Such thickenings should be neutralised before using in discharge pastes.

2. Whenever possible slightly alkaline discharge printing pastes should be used. It is recognised that this may involve a careful selection of dyes for use in producing the ground shades to ensure that the white discharge is not yellowed by such alkaline conditions, but there is a fairly wide choice of such dyes to-day from the various manufacturers. In the few cases where this is not possible steps should be taken to see that the printing paste is neutral and not acidic.

3. After printing, the materials should be well dried as speedily as possible.

4. After steaming, the goods should be washed off without undue delay. If the style is a single white discharge, the steaming conditions may be arranged with advantage to be drier than is normally sought for when producing vat colour prints.

If the above operating conditions are adhered to it is felt that there will be little risk of tendering in the production of discharge styles and, whilst it is not claimed that moisture, temperature of storing and acidic conditions are the only factors involved, they appear to be the main factors involved in practical printing. Further work remains to be carried out in the field, particularly on the effect of small amounts of metallic impurities on the catalytic decomposition of sodium formaldehyde-sulphoxylate and their effect on the production of free sulphoxylate or other anions or radicals during the process.

* * *

The authors wish to place on record their indebtedness to the Bleachers' Association Ltd. and to Messrs. James Hardcastle & Co. Ltd. for their co-operation in the practical side of this work, and for the facilities which have been placed at their disposal for the carrying out of the actual printing trials under works conditions.

Thanks are due also to Dr. W. Cule Davies and Mr. J. White of the Central Research Department, Brotherton & Co. Ltd., for help in this work and to the Directors of Brotherton & Co. Ltd. for permission to publish this paper.

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(MS. received 17th October 1953)

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Discussion

Mr. J. W. RUWHOF: What is the meaning of these results for processes like molten metal dyeing and pad-steam, in which sodium hydrosulphite is used?

Mr. R. J. HANNAY: The work described in this paper has no bearing on processes like the Stand-fast Molten Metal process or the pad-steam method in which sodium hydrosulphite is used as the reducing agent. This product is always used under alkaline conditions and we have never come

across any cases of tendering connected with the operation of such processes.

Mr. RUWHOF: I would like to draw the attention of Mr. Hannay to the work of Schönberger (*Melliand Textilber.*, **32**, 636-638 (1950)) who thought about a catalytic action of copper and iron salts. Did you find anything about that?

Mr. HANNAY: The work we have described has been confined to a study of the method of decomposition of Formosul under normal printing

conditions and has shown that it is possible to produce tendering of cellulose when using slightly acidic printing pastes under certain conditions of temperature and humidity. The catalytic effect of the presence of metals or metal salts such as those of copper or iron has not been studied. It may be that the tendering effect would be increased or speeded up by the presence of such metals in the print paste, but their presence is not essential for the production of tendering under the conditions we have described. Further work remains to be done, and this is one of the aspects that must be studied.

Mr. W. TAUSSIG*: After publication of a paper in 1943†, routine fluidity testing of white discharges on viscose was started. The bulk of the discharged fabrics proved to be absolutely satisfactory, but on one occasion it was found that the fluidity of the discharged part was 2½–3 units above the fluidity of the ground. This indicated that during the previous investigation some factor had been missed and that the problem required further investigation. A number of laboratory trials were carried out without bringing to light any facts which had not been observed previously. Finally, it was decided to carry out trials in bulk. Here it was found that if the material is allowed to lie in covered boxes for two to four days after steaming, particularly if the material was not cooled after steaming, the fluidity of the discharged parts rises. Material taken from the same printing, if washed off immediately after steaming, gave quite normal fluidity figures.

Having made this observation, an attempt was made to obtain the same result in the laboratory. Having found previously that lying of prints after steaming under normal conditions and also in a drying oven at a controlled temperature up to 80°C. for two days gave no noteworthy rise in fluidity of the discharge parts, the following trial was carried out—

A white discharge printed material was steamed and then divided into three parts, one part (No. 1) was hung in the lab., one part (No. 2) kept in drying oven at a controlled temperature of 80°C. and one part (No. 3) was put in a stoppered test tube containing 2 c.c. water. Care was taken that the material was not in direct contact with the water. This test tube was then put in the drying oven and kept at 80°C., along with part No. 2 for two days. Parts Nos. 1 and 2 showed no abnormal increase in fluidity but Part No. 3 gave a fluidity rise up to six points on the discharged parts. Later trials showed that a similar rise in fluidity occurred if printed but unsteamed material was allowed to be under the same conditions.

It seemed to be important at this stage to find whether the tendering was due to the formation of oxy- or hydro-cellulose, and in order to determine which of these was formed, trials were carried out. In these trials, bleached, unmercerised cotton was used in place of viscose, in order to avoid any error which might have been caused by starting with a material already fairly strongly degraded. Further, to eliminate any possibility of the dyed ground or

the thickening in the printing colour having any influence, the trials were carried out on white material by padding through an aqueous Formosul solution. Bleached, unmercerised cotton was padded through 200 g./l. Formosul, dried, steamed 10 minutes at approximately 102°C. and then kept for four days in a stoppered test tube containing 2 c.c. water at a temperature of 70°C. (Sample A). A part of the original material and a part of Sample A were boiled for six hours in 1% caustic soda solution, the loss in weight and fluidity then determined.

	Fluidity	Fluidity after Boil	Loss in Weight after Caustic Boil
Original Cotton	4.13	4.8	0.83%
Cotton (Sample A)	24.9	28.5	22.8%

It was also found that tendering occurs if the Formosul in the above trial is replaced by sodium bisulphite or sodium sulphite or sodium sulphate made alkaline with caustic soda.

The experiment was repeated, keeping the patterns in an atmosphere of coal gas and in this case no noteworthy tendering occurs. From these facts it was concluded that the tendering of the material was due to the formation of oxycellulose.

It seemed therefore remarkable that oxycellulose should be formed in the presence of such a strong reducing agent as Formosul, and an attempt was made to find out if the oxycellulose is formed after the whole of the Formosul has been oxidised or during the oxidation of the Formosul. To investigate this question the following trial was carried out. Bleached unmercerised cotton of fluidity 4.8 was padded with solutions of 300, 200 and 100 g./l. Formosul respectively, with mangle expression of approximately 100%, dried and kept in stoppered test tubes with 2 c.c. of water as previously but at 70°C. for 24, 48, and 96 hours. The fluidity figures are shown in the following graph.

Before estimating the fluidities the material was tested for residual reducing agent by means of a ferric thiocyanate solution. It was found that after 24 hours all patterns decolorised the ferric thiocyanate solution, after 48 hours the patterns padded with 300 and 200 g./l. Formosul still decolorised the ferric thiocyanate solution while the pattern with 100 g./l. Formosul did not. After 96 hours none of the patterns decolorised the ferric thiocyanate solution.

The conclusion is therefore that the degradation of the cotton starts while reducing agent is still present, and increasing the amount of reducing agent reduces the rate of this degradation. However, once the reducing agent has been oxidised, the degradation proceeds much more rapidly. The mechanism of the reactions involved during the tendering of cellulose by Formosul is very complicated and must be assumed to be due to auto-oxidation. It is worth noting that alkaline sulphite under similar conditions causes tendering similar to Formosul.

The facts thus established merely confirm the old experiences that a print containing a Formosul should be kept before and after steaming in a cool

* Communicated

† J.S.D.C., 59, 217 (1942).

and dry place and recommendations to cool material after printing and steaming are not without foundation.

Mr. W. FURNESS*: We wish to thank Mr. Taussig for his interesting observations, but would like to point out that the conditions under which his laboratory tests were made do not closely simulate those that are generally to be found in the discharge printing trade. The inclusion of sodium carbonate in printing-paste compositions will prevent the development of those circumstances which we believe to be most often the cause of tendering, but Mr. Taussig's remarks serve to remind us that tendering may sometimes be due to causes other than those traced in our own experiments.

Mr. H. WILSON: Has Mr. Hannay any knowledge of the cause of tendering on cotton goods dyed insoluble azo ground and white discharge with anthraquinone and alkali added. This connected with navy ground only not experienced with reds. Is there some intermolecular reaction with the azo dyestuff lake?

Mr. HANNAY: The lecturer has never experienced the type of tendering described, namely an effect produced when discharging navy blue grounds dyed with Brenthol AS and diazotised dianisidine. Discharges for such dyeings are usually highly alkaline and contain caustic soda. It would be interesting to know if any check was made on the unprinted cloth to determine if any over bleaching effect was present in the preparation. If so, the presence of caustic soda in the print paste, particularly under steamer conditions, might give rise to tendering.

Mr. H. A. TURNER: There seems to be some conflict of opinion between the authors and Mr. Taussig about the cause of modification of the fibre when formaldehyde-sulphoxylate decomposes in contact with it. Could not this be resolved, for any specified experimental conditions, by extending the chemical tests beyond the direct estimation of cuprammonium fluidity, which is, in the first instance, only a test for depolymerisation? Testing fluidity before and after a mild alkaline treatment, or determinations of copper number and carboxyl value should be sufficiently informative.

When the authors were investigating the decomposition of the formaldehyde-sulphoxylate, and especially when they were seeking to assess the significance of the changes which took place in the pH value, had they in mind the account of investigations by Kunin†? He found that the decomposition of solutions at 80°C. and below leads to a fall in pH, caused, it is suggested, by the formation of bisulphite and formic acid (resulting from a disproportionation reaction in the liberated formaldehyde), while at temperatures above 100°C. the pH rises, principally, it is claimed, through the hydrolysis of Na₂S.

Mr. FURNESS: Contrary to my reply at the Symposium, and with apologies to Mr. Turner for misunderstanding part of his question, the papers by Kunin had been consulted at the outset of this work and, as a result, sodium sulphide had been

added to some discharge pastes to encourage the formation of thioformaldehyde during steaming. This, however, did not lead to tendering.

The work of Kunin refers exclusively to the decomposition of sodium formaldehyde-sulphoxylate in aqueous solutions, and in our present work we have neither confirmed nor opposed his conclusions. There was so little difference between the pH values of aqueous extracts from steamed and unsteamed fents that we can find no justification for suggesting that formic acid might be produced during the steaming process. If it were supposed that formic acid is produced but volatilised during the passage through the steaming cabinet, appreciable quantities of free sulphite would have been left on the crêpe. In our experiments appreciable quantities of sulphite were formed only in the presence of sodium carbonate, and in those cases the explanation given in the text is preferred. As neither sodium sulphide nor sodium hydroxide were formed in appreciable quantities during the steaming process, the decomposition of sodium formaldehyde-sulphoxylate in discharge printing cannot be ascribed to other reactions of the type formulated by Kunin.

Prof. J. B. SPEAKMAN: As regards the work which the authors have carried out since the paper was submitted, it seems possible that too much stress may have been given to acidic conditions as a *direct* cause of tendering. Conversely, insufficient attention may have been given to free radical formation, which may well be important in the redox system under investigation. A possible means of discovering whether free radical formation is more likely under acidic than under alkaline conditions would be to include a monomer, such as methyl methacrylate, in the printing paste and study the conditions under which polymerisation takes place most readily.

Mr. HANNAY: The authors are grateful to Professor Speakman for his suggestions. As pointed out earlier in the discussion, the work is not complete and investigation of this aspect of the problem has still to be carried out.

Mr. F. CROMPTON*: On the remarks by Mr. Taussig. Does the addition of Zn oxide cause tendering on cotton if left in a moist condition similar to the tendering mentioned on viscose?

Mr. HANNAY*: As far as we are aware at present, the addition of zinc oxide to the discharge print paste has no tendering effect on cotton in the discharge process. It must be remembered, however, that the presence of zinc oxide or of titanium dioxide, which is also used, in the prints after washing off and finishing can give rise to serious light tendering in curtain materials or fabrics which are subject to strong light exposure.

Mr. J. F. MASTERS*: Have the authors any experience with the use of the optical bleaches for enhancing the white discharge? Or does the fact that these are substantive obviate their use?

Mr. HANNAY*: The inclusion of small amounts of optical whitening agents in the print paste has frequently been used in the production of white discharges and tends to brighten the resulting

† J.S.D.C., 66, 246 (1949); 66, 62 (1950).

discharge effect. An alternative method, particularly useful when pale bright ground shades are desired, is to add the optical whitening agent to the dyebath, where it is dyed on the fabric along with the colour. In printing it is not affected by the discharge paste.

Mr. R. HOLDEN*: Some evidence that free radicals are present when Formosul is oxidised on cellulose has been obtained by impregnating spun viscose rayon fabric with a solution of neutral Formosul to which naphthalene sodium sulphonate had been added. The impregnated fabric was stored in a moist atmosphere at room temperature for several hours, and then treated with an excess of diazotised sulphanilic acid, whereupon a pink colour developed. This pink colour can only have arisen by the coupling of the diazotised sulphanilic acid with a naphthol derived from the naphthalene sulphonate. It is difficult to conceive any way in which hydroxyl groups can have been introduced into the naphthalene sulphonate except by means of free hydroxyl radicals (compare Weiss and Stein^{1, 2}), and it must therefore be concluded that

free hydroxyl radicals are produced during the simultaneous oxidation of Formosul and cellulose during the storage of the impregnated material. It is noteworthy that the pink colour does not develop if a cellulose fabric is replaced by a glass one, although the Formosul is oxidised to similar products on both substrates. No evidence either of the oxidation of cellulose or of the existence of free radicals has been obtained when sodium sulphite is oxidised on cellulose in this manner.

Mr. FURNESS*: Mr. Holden has introduced an aspect of the subject which is new to us, and we thank him for his contribution. In the presence of traces of copper, iron, nickel, cobalt, or other metals that have more than one valency state we think it probable that the decomposition of sodium formaldehyde-sulphoxylate would be accompanied by formation of some free radicals. In the absence of such metals, however, we are unable to explain why free OH radicals should be produced specifically by the decomposition of the formaldehyde-sulphoxylate ion on cellulose whilst sodium sulphite on cellulose yields none.

¹ Weiss and Stein, *Nature*, 1948, **161**, 650.

² Weiss and Stein, *J.C.S.*, 1949, p. 2074.

Thiourea Dioxide (Formamidinesulphinic Acid) A New Reducing Agent for Textile Printing

P. KRUG

Thiourea dioxide, an oxidation product of thiourea, is a reducing agent which is stable both in solid form and in cold aqueous solution. It has a slight acidic reaction, and acquires full reducing power only when heated in aqueous solution to about 100°C. This paper briefly describes the chemistry of thiourea dioxide, and deals with it as a reducing agent for vat dyes in the direct and discharge printing of cellulose acetate, silk, and wool. Owing to its acidic properties, these fibres can be printed with a minimum of degradation and great safety of production. The new reducing agent has been tried on a practical scale, and results of trials are demonstrated.

Thiourea dioxide or formamidinesulphinic acid was first prepared and described by Barnett¹ in 1910, but it remained a laboratory curiosity until 1939, when Lubs of the du Pont organisation discovered its potential use as a reducing agent in textile applications. Their patent² covers a wide field of uses for thiourea dioxide, such as dyeing and printing with vat dyes, discharge printing, stripping, and a modification of the pad-dyeing method with vat dyes. It appears that the inventors considered alkali to be essential either for the reduction of vat dyes by means of thiourea dioxide or for its action as a stripping and discharging agent. In the course of this paper, however, it will be shown that under alkaline conditions thiourea dioxide behaves very similarly to sodium dithionite (hydrosulphite), and that no great practical advantages can be gained by its use in an alkaline medium.

Some years later the Celanese Corporation of America³ described the use of thiourea dioxide for the production of vat-coloured discharges on suitably dyed cellulose acetate, but it again appears that stress was placed on the alkalinity of the printing colours. An interesting use for thiourea dioxide was also suggested by the former I.G.⁴, viz. as an antioxidant for certain Indigosols which are sensitive to nitrous acid.

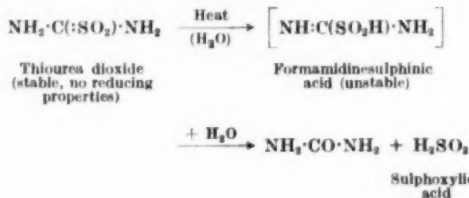
Nevertheless, thiourea dioxide remained a laboratory curiosity despite a few patents for its production and application. Mr. G. Sutton⁵, who was interested in the dyeing of cellulose acetate, drew our attention to the possibilities of the use of thiourea dioxide, and our earlier work on printing was done in collaboration with him.

Thiourea dioxide is, as the name implies, an oxidation product of thiourea. We were attracted by the possibilities of developing a new reducing agent from thiourea which promised to have somewhat similar properties to the reducing agents commonly used in the textile field. It was soon realised that thiourea dioxide was an interesting chemical in that it did not require alkaline conditions in order to act as a reducing agent either for vat dyes or for discharge printing. On the contrary, it was found that it could develop a strong reducing action also under acidic conditions, and, furthermore, that it was then much more stable. We have been able to establish the conditions under which thiourea dioxide—or Manofast, under which name it is marketed—can be used with advantage.

Below is given a description of the chemical properties of thiourea dioxide and of its behaviour as a reducing agent in textile printing.

CHEMICAL PROPERTIES

Thiourea dioxide is produced by the oxidation of thiourea with hydrogen peroxide. Judged by the method of its production, it might be expected to have the properties of a peroxide, and least of all would it be expected to be a reducing agent. These properties can be explained by the theory that it exists in two isomeric forms, one stable and the other exceedingly unstable, the latter being the form which acts as a reducing agent. As a solid it has neither oxidising nor reducing properties, is practically inert to most chemical reagents, and is insoluble in the common organic solvents. Although it contains two amino groups, no reaction occurs with such reagents as acid chlorides or acid anhydrides. With alkalis in the cold, and on heating in aqueous solution, re-arrangement takes place, giving a product which has reducing properties. The structure of the new compound is probably that of a sulphinic acid. This re-arrangement is irreversible, and acidification of the sodium salt produced by the alkaline treatment of thiourea dioxide does not give the original product. Complete decomposition takes place, and one of the by-products of this decomposition is sulphonylic acid, which acts as the reducing agent—



Aqueous solutions of thiourea dioxide show a slightly acidic reaction of pH 5 and are very stable at 20–30°C. On heating, however, the thiourea dioxide is converted into formamidinesulphinic acid, which is unknown in the free state and which acts as a reducing agent by virtue of its conversion into sulphonylic acid.

Thus alkaline conditions convert thiourea dioxide into an unstable reducing agent having similar properties to sodium sulphyxylate. Acidic solutions, however, show great stability and develop reducing power only at elevated temperatures,

particularly around 100°C. in presence of moist saturated steam. These properties of thiourea dioxide evidently make it valuable for textile printing, and the comparison between Manofast and sodium formaldehyde-sulphoxylate is obvious: whereas the latter is stable under alkaline conditions, the former is exceedingly stable when acidic, and acquires its full reducing properties only when subjected to steaming on the cloth. Because of its somewhat higher cost than hydrosulphite, Manofast is of interest principally as an acidic reducing agent.

The solubility of thiourea dioxide in water at 20°C. is approx. 3%, but increases rapidly with rise in temperature. As concentrations which are somewhat higher than the solubility are recommended in recipes for printing by either screen or roller, particularly the latter, it follows that part of the Manofast will be in suspension in the colour paste. Fortunately, it has been found that this has no deleterious effect on the results, especially when thickening agents of the British-gum type are used. The particle size of Manofast is very small and sedimentation in the printing paste slow. No tendency to crystallise out or to damage the printing rollers mechanically has been experienced.

Comparative stability tests of aqueous solutions of Manofast and formaldehyde-sulphoxylate have established the greater stability of the former. Equal weights of the two reducing agents were placed in two dry flasks, and a piece of cloth of the same surface area put in each flask, thus causing a greater surface to be exposed to oxygen. The air was swept out with oxygen, the same volume of water added to each flask, and the flasks immediately connected to mercury manometers and allowed to stand for several days at room temperature. The decrease of pressure was noted for both flasks.

TABLE I
Formaldehyde-
sulphoxylate

Weight, g.	2.008	Thiourea Dioxide	2.009
Initial vol. of O ₂ , c.c.	340		336
Time	Pressure Decrease (cm. Hg)		
0	0		0
1 hr.	0		0
2	0.3		0
4	0.9	Slight excess pressure	
6	2.3	Slight excess pressure	
1 day	18.0		0.8
2 days	32.7		0.3
4	43.5		0
5	46.6		0.1
7	48.9		0.8
8	50.0		2.5
9	48.0		3.1
10	48.7		2.0
14	49.6		—
Vol. of O ₂ finally absorbed, c.c.	238.4		~0

The pressure decrease is directly related to the stability of the two compounds, and it is seen from Table I that the stability of aqueous Manofast far exceeds that of formaldehyde-sulphoxylate. The latter decomposed at a steady rate up to ten days, finally absorbing two atoms of oxygen per molecule.

Manofast absorbed a negligibly small volume of oxygen over the same period.

The results of these laboratory experiments were borne out by practical trials, in which prints containing Manofast were kept for indefinite periods before steaming without any sign of decomposition being noticed. This point will be particularly appreciated by screen or hand-block printers. Practical experiments have also revealed that the stability before ageing of prints made with Manofast is considerably better than that of those containing zinc formaldehyde-sulphoxylate. We have recently had occasion to carry out some discharge printing of wool by means of Manofast, and for the sake of interest kept a small cutting for two months before steaming. There was no change whatsoever in the colour yield, whereas comparative prints made with zinc formaldehyde-sulphoxylate were useless because of the decomposition of the reducing agent.

MANOFAST AND VAT DYES

When a printing paste containing a vat dye, Manofast, and a suitable thickening agent is printed on to a textile material, and subjected, after drying, to a steaming with saturated steam at 100–102°C., then in most cases reduction to the free leuco vat acid takes place in good yield. Many of the vat acids have affinity for acetate rayon, wool, and silk, and it thus becomes possible to achieve fixation of vat dyes on these fibres in excellent yields and under acidic conditions with no saponification or very little damage to the fibres. Practical results have been achieved on an industrial scale on all three fibres by screen, roller, and hand-block, in direct and discharge printing.

PRINTING OF ACETATE RAYON

Although the majority of vat dyes are reduced to the vat acids by the Manofast method, not all of them have affinity for acetate rayon. As would be expected, a great number of the indigoid, thioindigoid, mixed indigoid-thioindigoid, and indolenaphthalene indigoid dyes are specially well suited and give very good colour yields. In addition, there are a fair number of anthraquinonoid dyes which give very satisfactory results by the method, such as—

Caledon Printing Yellow GKS	...	ICI
Caledon Yellow 2RS	...	ICI
Cibanone Golden Yellow RK	...	Ciba
Indanthren Yellow 4GF	...	Basf
Indanthren Yellow 7GK	...	Basf
Indanthren Yellow GGF	...	CFM
Anthra Yellow GGC	...	Basf
Caledon Gold Orange G	...	ICI
Indanthren Brilliant Orange RR	...	FH
Caledon Dark Blue G	...	ICI
Indanthren Navy Blue RR	...	Basf
Alizaranthrene Navy Blue R	...	ICI
Caledon Printing Purple 4R	...	ICI
Caledon Jade Green brands	...	ICI
Indanthren Grey BG	...	FBy
Indanthren Grey 2G	...	Basf
Caledon Printing Grey 3B	...	ICI
Indanthren Brilliant Green H3G	...	FH

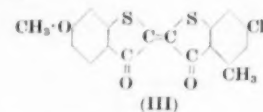
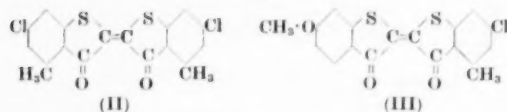
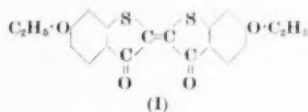
In addition, medium colour yields can also be obtained with the following dyes—

Caledon Printing Orange 2RT	...	ICI
Caledon Brilliant Red 3B	...	ICI
Caledon Printing Olive Green B	...	ICI
Indanthren Red Brown R	...	Basf

Dyes of the indanthrone series give rather poor results, but Caledon Blue XRC can be used for the production of light-fast sky blues. For the production of deeper blues of excellent light fastness, we recommend the use of Caledon Dark Blue G, which on acetate rayon yields very much brighter prints than on cotton or viscose rayon. The following dyes of the non-anthraquinonoid type are particularly recommended because of their good colour yields and bright prints—

Durindone Printing Scarlet Y	...	ICI
Indanthren Scarlet B Suprafix	...	CFM
Ciba Brilliant Pink 2BG	...	Ciba
Ciba Red B	...	Ciba
Indanthren Printing Red 3B	...	CFM
Ciba Bordeaux 2RN	...	Ciba
Durindone Printing Red 3B	...	ICI
Ciba Violet 6R	...	Ciba
Indanthren Printing Violet BBF	...	CFM
Ciba Blue 2B	...	Ciba
Indanthren Printing Blue GG Suprafix	...	FH
Ciba Red Brown R	...	Ciba
Ciba Brown G	...	Ciba
Ciba Brown 2B	...	Ciba
Ciba Black BL	...	Ciba
Indanthren Printing Black B Suprafix	...	FH

It is very interesting to note that the symmetrical thioindigo dyes like Algol Orange RF (CFM) (I) and Indanthren Brilliant Pink R (CFM) (II) do not give satisfactory colour yields by the method, and neither do mechanical mixtures of the two products. If the molecule is unsymmetrical, as in Indanthren Scarlet B (III), then excellent colour yields are obtained. The prints have a light-fastness rating of 6-7.



LIGHT FASTNESS

Particular attention was given to the study of the light fastness of vat dyes printed on acetate rayon by the Manofast method. Comparatively little was found in the literature about this point, probably because the existing methods of printing acetate rayon have not been very successful, and are mostly based on saponification of the fabric. All light-fastness assessments were therefore likely to be largely interpretations of light fastness on viscose rayon. We are very greatly indebted to Imperial Chemical Industries Ltd., Dyestuffs Division, who have studied the problem of the light fastness of vat dyes on acetate rayon, and who drew our attention to the importance of soaping the prints at temperatures of about 70°C. The importance of this after-treatment for the light fastness appears to be

greater in the case of acetate rayon than it is for cotton or viscose rayon. It can be well illustrated by the example of Ciba Brown G, which has a light fastness of 2 when soaped at 50°C., and 7 when soaped at 70°C. A number of vat dyes have a better light fastness on acetate than on viscose rayon, provided they are properly soaped, and a good range of dyes is available the light fastness of which could be deemed sufficient even for furnishing materials. Our work has also included attempts to produce bright lime greens of outstanding light fastness, a problem which is ever present—also on cotton—and excellent results have been achieved with a combination of Cibanone Golden Yellow RK (Ciba) and Indanthren Brilliant Green H3G Suprafix (FH).

With the existing range of applicable vat dyes, we are now in a position to match all the shades obtainable on acetate rayon by the disperse type of dyes, with superior light fastness in practically all cases.

Other Fastness Properties

The other fastness properties on acetate rayon correspond roughly to those obtained on cellulosic fibres and can therefore be described as excellent. Many thousands of yards of various types of acetate rayon cloth have already been processed by the Manofast method, and the fastness to rubbing has been, in all cases, very good.

Method of Printing

For the printing of acetate rayon, a vat dye, Manofast, and a thickener are applied in conjunction with a suitable swelling agent in order to ensure good colour yield, penetration, and fastness to rubbing. It will be appreciated that, as a consequence of the application of a swelling agent, some loss in tensile strength of acetate rayon ensues, but this is well below the limit of what is commercially accepted. On the majority of cloths which we have processed the loss is of the order of 10%. Combinations of polyethylene glycol (mol. wt. 200) and urea for screen printing, and of polyethylene glycol and thiodiethylene glycol for roller printing, have been found especially suitable.

Colour pastes containing vat dye, Manofast, thickener, and swelling agent are stable when kept in a cool place, although some prereluction takes place with easily reducible dyes, in the course of which the acidity of the printing paste appears to be slightly increased, and this retards further reduction. One of the dyes which is exceptionally easy to reduce, viz. Caledon Printing Yellow GKS, was tested for stability in conjunction with Manofast; although prereluction occurred, there was no loss in colour yield after the paste had been kept for over a month.

After being dried, the prints are steamed with saturated steam at 100-102°C. in the normal type of equipment. Pressure steaming should be avoided because of the possible adverse effect upon the strength of the material, even in the absence of any ingredient of the printing paste. It has been found, for example, that an acetate rayon fabric which had been steamed for only 3 min. at 20 lb./sq.in. had lost over 40% of its tensile strength.

After being steamed, the prints are thoroughly rinsed in cold water and then oxidised with sodium nitrite and sulphuric acid in a manner analogous to the solubilised vat dyes. Only in cases of discharge printing where the ground dyeings might be susceptible to nitrous acid is an oxidation with sodium percarbonate or hydrogen peroxide preferable.

In the rinsing process after the steaming, all the excess of dye, thickener, and swelling agent is removed, and since the excess of dye is in the form of the vat acid with no affinity for the fibre in the cold, no discoloration of the white ground can occur. This factor—the preservation of a perfectly white ground—constitutes one of the major advantages of the Manofast method, as it has previously caused considerable difficulties when disperse dyes are used.

The main advantages of the method can now be summarised as follows—safe production of vat-dye prints on acetate rayon having excellent brightness of shade, without saponification of the cloth and without danger of discoloration of whites or of marking off. The range of dyes applicable by the method is extensive enough to permit the production of all shades with the highest fastness properties.

Discharge Printing

The production of discharge prints on acetate rayon cloth has presented the printer with considerable difficulties. Alkaline discharging agents not only cause saponification of the cloth and impair the handle, but also give rise to haloing, flushing, and, in the case of vat-illuminated discharges, mottled prints. Some of the acidic alkaline-earth sulphonylates which are recommended for the production of discharge prints on acetate rayon have a tendency to crystallise out in the printing paste, thus causing damage to and scratches on copper rollers. This is particularly the case when dark shades have to be discharged. Furthermore, the colour yields are rather low when vat dyes are used for illuminating effects, and some dyes lack brightness. It has always been realised that satisfactory discharge effects can be achieved on acetate rayon only under acidic conditions, and it is interesting to quote a modification suggested by the former I.G.⁶ for the production of these styles. A normal formaldehyde-sulphonylate vat dye printing paste is recommended to contain an addition of diethyl tartrate, which on steaming liberates tartaric acid. The alkalinity of the colour paste is thus eliminated during steaming, saponification of the acetate rayon is practically completely avoided, and the vat dyes are absorbed by the cloth in the form of the free leuco compounds. This method clearly foreshadows the application of free leuco compounds of vat dyes to alkali-sensitive textile materials. Its practical exploitation, however, has not been successful, partly owing to insufficient stability of either printing pastes or prints before ageing. In addition the colour yields seem to be rather poor.

The problem of obtaining the required acidic conditions for the discharge printing of acetate rayon seems to have found a satisfactory solution in

the use of Manofast. As illustrated by our patterns, white or coloured discharges can now be obtained with safety, even on dark shades, in screen and roller printing. An addition of zinc sulphate is recommended for the production of white discharges, as it seems to catalyse the reducing action of Manofast. For coloured discharges and vat-illuminated work, the omission of zinc sulphate is, however, advisable, particularly for heavy shades, as it slightly decreases the colour yield. Practically the same method as that applied for direct printing is recommended for discharge printing. The addition of urea has been shown to be of advantage for improvement of penetration.

It is to be hoped that the ease with which coloured discharge effects can now be produced will encourage the dye manufacturers to complete their series of dischargeable products: there is still neither a dischargeable blue of good light fastness nor a dischargeable black.

PRINTING OF WOOL AND SILK

Since a number of free leuco vat acids having affinity for wool and silk can be obtained in excellent yields by using Manofast as the reducing agent, the method offers a very convenient and economical way for the application of vat dyes to these fibres. The possibility of applying them to wool under slightly acidic conditions means that the damage to the fibre can be reduced to a minimum (about 10% loss in tensile strength), and the method affords a great degree of safety. Until the advent of Manofast no entirely satisfactory method has existed for the production of vat-dye prints on protein fibres, particularly wool. The method of application is practically the same as that outlined for acetate rayon, except that a small addition of Solution Salt SV is recommended, as in many cases it considerably improves the colour yield. A typical recipe is as follows—

SCREEN PRINTING	
10–20%	Dye
5%	Manofast
10%	Polyethylene glycol
3%	Solution Salt SV (ICI)
20–40%	Water
52%	British gum

Polyethylene glycol, which has been recommended as a swelling agent for the printing of acetate rayon, has been found to be a very useful auxiliary for the printing of wool by the Manofast method, providing the required hygroscopicity for the steaming operation. The prints are steamed in the usual way for 8–10 min. with saturated steam at 100–102°C., then rinsed in cold water, oxidised with hydrogen peroxide and ammonia or sodium percarbonate at 60°C., and finally soaped. As would be expected, the indigo or thioindigo types of dyes are foremost in the affinity of their free leuco compounds for wool and silk. Also, these dyes have excellent light fastness on wool, and a complete range of light-fast shades can now be obtained on that fibre by means of Manofast. Following is a list of those indigoid or thioindigoid dyes which give particularly good results on protein fibres—

Durindone Printing Scarlet Y	...	ICI
Ciba Red B	...	Ciba
Ciba Brilliant Pink 2BG	...	Ciba
Durindone Printing Red 3B	...	ICI
Indanthren Printing Red 3B	...	CFM
Ciba Violet 6R	...	Ciba
Durindone Red B	...	ICI
Ciba Violet 2R	...	Ciba
Indanthren Printing Violet BBF	...	CFM
Ciba Blue 2B	...	Ciba
Ciba Brown G	...	Ciba
Ciba Brown 2B	...	Ciba
Ciba Black BL	...	Ciba
Durindone Printing Black AN	...	ICI
Indanthren Printing Black B	...	FH

In addition, the following anthraquinonoid products give very good results—

Caledon Printing Yellow GKS	...	ICI
Indanthren Brilliant Orange 2R Suprafix	...	FH
Caledon Printing Jade Green XN	...	ICI
Indanthren Brilliant Green H3G	...	FH

Discharge Printing of Wool and Silk

The discharge printing of these fibres follows the same lines as those given for the application of vat dyes. For the production of good whites an addition of zinc sulphate is recommended, and excellent results are achieved, especially on wool which has been dyed with metal-complex acid dyes (Ultralans (ICI), Neolans (Ciba), or Palatine Fast (BASF)). The degradation of the wool is reduced to a minimum. When the formaldehyde-sulphoxylates are used for discharge printing, a considerable excess has to be applied in order to counteract their tendency to decompose. This excess is responsible in many cases for damage to the fibre. Owing to the stability of Manofast, almost theoretical quantities are sufficient to produce a good discharge effect, and 2–5% of

Manofast in the printing paste will, in most cases, produce the required results with a minimum of fibre degradation. Colour discharges on these materials could also be produced by means of vat dyes, but this will not be necessary in all cases, because those acid or chrome dyes which are resistant to reducing agents will probably meet all the requirements.

MIXED FABRICS

Very good results can be obtained by the Manofast method either in direct vat-dye or discharge printing on mixed fabrics consisting of fibres having affinity for leuco vat acids, such as acetate rayon-silk and acetate rayon-wool. The latter fabric has now been printed very successfully as a print-on style with vat dyes, and as a vat-dye discharge print on a knitted fabric which had previously been dyed with a mixture of dischargeable disperse and chrome-complex dyes. This latter print represents a novel development of some possibilities.

Whilst the new technique of reduction under acid conditions with thiourea dioxide to give leuco vat acid has been developed so far only on acetate rayon, wool, and silk, it is hoped that the method will find industrial application to other textile materials.

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(MS. received 12th June 1953)

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Discussion

MR. R. J. HANNAY: Dr. Krug in his paper has mentioned the suitability of thiourea dioxide for roller printing, and at the same time under the section on chemical properties has drawn attention to its conversion to the unstable formamidinesulphinic acid under the influence of heat and moisture. The results of investigations which we have carried out indicate that the temperature at which this conversion takes place is of the order of 40°C., and that at temperatures above this, the product is extremely unstable when in aqueous solution. Printing trials have shown that print pastes containing thiourea dioxide must be prepared at temperatures well below 40°C. if loss of reducing power is to be avoided, and secondly that the drying of fabrics after printing and before steaming must also be carried out at temperatures not exceeding 40°C. If prints are dried over steam-heated copper cylinders in the normal manner as on the standard roller printing machine, very poor results are obtained, and to reduce the drying temperature to safe limits would mean a very appreciable loss of production from the machine, unless a very lengthy drying system was installed.

Dr. P. KRUG: We agree that printing paste containing Manofast should be prepared and kept

at temperatures below 40°C. As to the application in roller printing, lapping of cylinders or a hot air drying method is recommended. Cellulose acetate being a hydrophobic fibre requires very much less drying than fibres like cotton and thus drying can be easily controlled.

Many thousands of yards of cellulose acetate cloth have already been processed in roller printing, and we have not encountered any difficulties where the drying has been controlled. Once the printed cloth has been dried under controlled conditions it can come into contact with steam-heated copper cylinders.

We have had the experience that during stoppages the print thus dried had to be left for a long period on a steam-heated copper cylinder, but no decrease of colour yield was noticed.

MR. J. C. OSTLE: White discharge effects are never as good on nylon as on acetate rayon. Could the author suggest means of improving results on nylon?

Dr. P. KRUG: The addition of a swelling agent will improve the discharge effects on nylon. We suggest either ammonium thiocyanate or thiourea. Much will depend, of course, on the dyes used for the dyeing of the nylon and on the nylon cloth

itself. We have found it rather difficult to fix titanium dioxide on certain types of nylon; where this can be done the white will, of course, be considerably improved.

Mr. W. FURNESS: As an analytical chemist I am interested in the reactions formulated by Dr. Krug to explain the rearrangement of thiourea and the mechanism of decomposition of formamidine sulphinic acid. I should like to ask whether urea has been isolated from the decomposition products, and whether there is direct evidence of the intervention of sulphylic acid in reduction processes?

Dr. KRUG: Decomposition of formamidine sulphinic acid or thiourea dioxide is a rather complex reaction. However, urea has been identified as one of the decomposition products when formamidine sulphinic acid is decomposed under acidic conditions. The urea has been identified as the xanthidrol addition compound. No experimental evidence for the intermediate formation of sulphylic acid can be given, but the sulphur in the decomposition products can be identified as SO_2 .

Mr. R. K. FOURNESS: The conditions of soaping recommended for the vat colour discharges are somewhat severe. Has it not been difficult to find disperse dyes of suitable soaping fastness for the ground? Alternatively is modification of the treatment for increasing the light fastness of the vat dye possible?

Dr. KRUG: We agree that the conditions of soaping in order to achieve the best light-fastness are rather severe, but for colour discharges milder soaping conditions will, in most cases, be sufficient. Soaping at 50°C. to 60°C. and with selected vat dyestuffs will generally produce sufficient light-fastness to be equal to the light-fastness of the ground shades. The majority of dyestuffs which we have tried will withstand a soaping at 60°C. reasonably well.

Mr. K. LOWIT: When fixing vat dyes by the Manofast method on nylon, is it advisable to improve light fastness by pressure steaming after the dyes are fixed?

Dr. KRUG: It is known that the light fastness of vat dyes on nylon can be improved by pressure steaming. Such a steaming has, however, an adverse effect on the fastness to rubbing, because migration of the dye particles to the surface of the fibre takes place. As far as we know, the method is not recommended, and we have not tried it in connection with the Manofast process.

Mr. H. A. TURNER: In the series of reactions preceding oxidation, Dr. Krug states that urea is liberated. Does this substance, by acting as a "carrier", contribute to the ease of diffusion of free leuco compounds (vat acids) into fibres like cellulose acetate?

Dr. KRUG: In our recipes for screen printing we recommend the use of 5% Manofast. On decomposition this will yield about 2½% urea if the reaction proceeds quantitatively, which it probably never does. In our opinion this quantity of urea is not high enough to contribute fundamentally to the transfer of dyestuffs into the fibre.

Mr. J. M. PRESTON: The quantity of urea, 2½%, said to be liberated by Dr. Krug is, according to work we are doing, sufficient to increase the swelling of cellulose and the rate of diffusion of dyes into it.

Dr. KRUG: Quantities of 2½% of urea will no doubt exert a swelling action on the cellulose acetate fibre, but this action is not strong enough to provide for good colour yields. In comparison to 6% polyethylene glycol, which we recommend, or mixtures of polyethylene glycol and Glydote B, the colour yields are very much inferior.

Mr. PRESTON: Dr. Krug's statement that polyethylene glycols are more effective than urea in increasing colour yield cannot be due to their swelling action since they have exactly the opposite effect to urea and reduce the swelling of cellulose.

Dr. KRUG: We have found that polyethylene glycol on its own is not a very good swelling agent, but in conjunction with Glydote B is very effective. It is possible that there is a synergic connection of both these chemicals. It may be that polyethylene glycol acts partly as a solvent for the free leuco compounds of the vat dyestuffs.

Mr. A. N. RUSSELL*: Has the stability of optical bleaching agents in formamidinesulphinic acid discharge pastes been tested and if any have been found stable, have they been effective in improving the white?

Dr. KRUG*: As far as we are aware, the great majority of optical bleaching agents are stable to reducing agents, and this also includes formamidine sulphinic acid. We have tested Tinopal WG in the discharge printing of wool, and we have not only seen that it was completely stable in the presence of formamidine sulphinic acid, but that it also gave an improved white discharge effect.

* Communicated

Fast-to-light Basic Prints on Viscose Rayon

W. S. MILLER

In the past the brightest prints on viscose rayon have been obtained with acid and direct dyes, but these lack washing fastness, and many of the brightest acid dyes are also fugitive to light. The author shows how basic dyes, hitherto notoriously fugitive to light, may be printed by a new all-in method, resulting in the deposition within the fibres of colour lakes of molybdophosphoric acid. A number of stages in the development of this new printing technique are described, and are related to the earlier development of the manufacture of similar lakes in pigment form. The new prints are fast to light and washing, and may be supplemented where necessary by use of insoluble azo dyes applied by suitable methods.

When fabrics made from viscose rayon were first introduced they had many defects, but since the early days the manufacturers responsible for each stage of production, right down to the finished article, have minimised or even eliminated some of these defects, until to-day viscose rayon, by reason of its quality and durability as a fabric, occupies an important position in the textile industries of the world. First intended as a substitute for silk, it now stands on its own merits and is also finding increasing use as a substitute for other fibres such as cotton and in blending with many fibres. Among the improvements necessary to achieve such results, dyeing and printing have not been neglected, and great progress has been made in the direction of excellent all-round colour fastness. To-day vat dyes supplemented by such oxidation dyes as aniline black and certain insoluble azo combinations are in general use for direct print-on styles.

Vat-dye prints, however, lack the richness, clarity, and above all brilliance of colour which are generally associated with prints on silk. Attempts, successful in so far as appearance is concerned, have been made to produce silk-like prints by use of selected acid and direct dyes¹. This practice started with screen work, and was later adapted to machine printing, the process in general use consisting in printing a thickened aqueous solution of the acid or direct dye containing a proportion of a hygroscopic substance, usually urea, then drying, and steaming under moist conditions for 30–60 min. or longer. The prints are afterwards carefully washed to remove the thickening together with the urea and loose surface colour, and are finally dried and finished in any desired fashion. Great richness and brilliance of colour are thereby obtained, but fastness to washing is in general very poor and fastness to light varies according to the individual dyes. Owing to the lack of extreme brightness of direct dyes in the blue-violet-purple range, the colourist is obliged to use loose-to-light acid dyes for this part of his range. One cannot have many multicolour prints excluding blues, violets, and purples, and so it is obvious that this style cannot in general be classed as fast to light unless brilliance is sacrificed by using the faster but very much duller blues, violets, and purples to be found among direct dyes. The object of using acid and direct dyes, namely brilliant colourings, is thereby partly defeated.

Viscose is the most widely used rayon, and a multicolour print in vat dyes possesses a durability of colour which is more than satisfactory for all commercial purposes. If a greater resemblance to

silk is aimed at, then printing viscose rayon with acid dyes is not a real solution to the problem, because the fastness to both light and washing of such prints is much inferior to that shown by the same dyes when applied to silk, and even here there is room for improvement. Washing fastness can, it is true, be increased by various after-treatments, e.g. with a synthetic resin, but the problem is only half solved thereby. The present research was undertaken with a view to finding a method of producing exceptionally bright multicolour prints on viscose rayon fabrics, possessing fastness to light and washing at least approaching those of vat dyes.

The position at the inception of the work to be described in this paper can be briefly summarised thus—one could either have fast colours which were dull, or bright colours which were loose, certain insoluble azo dyes being exceptional in combining the virtues of fastness and brightness. There were therefore two possible lines of approach—namely to make dull fast dyes such as vats brighter, or to make bright loose dyes such as basics faster. In 1890 J. J. Hummel², in an address to the British Association, clearly thought very little of the second alternative, saying: "Not infrequently one is asked if there is no method of rendering the fugitive colours fast. The author's answer is—No! The fast or fugitive character of a colour is an inherent property of the colouring matter used, and dependent mainly, if not entirely, upon its chemical constitution."

Basic dyes at one time occupied a particularly important position in the field of calico printing by reason of the outstanding brilliance, bloom, and purity of the hues obtainable thereby. Their popularity has suffered a big decline in recent years owing to their poor light fastness and the increased demand for the vastly superior all-round fastness offered by vat and insoluble azo dyes. To-day the use of basic dyes is limited to a few special styles where requirements of brightness outweigh considerations of fastness. As commercial interest has waned, so technological development has slowed down, and for some years, now, publication of new and original researches into the printing of basic dyes has practically ceased.

The decision to attempt to make basic dyes fast to light was influenced by the knowledge that they yield lakes of excellent fastness when precipitated by complex acids of molybdenum and tungsten. It was thus necessary to devise means whereby similar lakes could be formed inside the fibre, in

predetermined areas of a fabric, without damaging the cellulose.

PREVIOUS WORK ON DYE LAKES OF MOLYBDENUM AND TUNGSTEN

In order to appreciate more fully the development of the textile printing process to be described, it is necessary to have some background knowledge of tungstophosphoric (phosphotungstic) lakes as first discovered and developed during the past forty years. It will be seen how much of this knowledge proved valuable in determining the best conditions for printing, though in certain points the claims of the lake-makers proved inapplicable.

First to disclose the production of lakes based on complexes containing tungsten and/or molybdenum were the Badische Anilin- und Soda-Fabrik, who in 1913 applied for a patent to cover the manufacture of new coloured lakes by precipitation of basic dyes with phosphometatungstic acid or its salts³. A patent of addition⁴ extended the process to the use of other complex acids of tungsten and the analogous molybdic acids. Shortly afterwards F. Bayer & Co. filed an application in which it was proposed to treat dyeings and lakes produced from acid dyes containing both sulpho and amino groups with complex acids containing tungsten, the object being to improve their light fastness⁵. Tungstophosphoric, -silicic, and -antimonic acids are quoted as being suitable for this purpose.

Lendle described similar processes for both basic⁶ and acid⁷ dyes, while Linz⁸ disclosed the production of tungsten lakes by precipitation of suitable colouring matters with a soluble compound of tungsten, a soluble compound of phosphorus, and a suitable acid capable of forming a double salt of tungsten in presence of the dye. As in the previous processes, the final product is a tungstophosphoric acid lake.

An I.G. Farbenindustrie AG. process made use of molybdenum for lake manufacture, and here basic dyes were precipitated from solution on to suitable substrates by addition of ammonium molybdate solution, either alone or together with sodium phosphate. Precipitation was completed by acidification, and the resultant lakes were claimed to have particularly good light fastness⁹. A further patent¹⁰ covered an analogous process with the soluble molybdate replaced by a soluble tungstate: e.g. a basic or an acid dye was precipitated from solution on to a suitable substrate, and solutions of sodium tungstate, sodium phosphate, and an acid of a greater degree of dissociation than tartaric acid were successively added in order to complete the formation of a fast-to-light lake.

Another development featured the use of complex acids containing both molybdenum and tungsten, for the manufacture of lakes and the treatment of dyeings of acid and basic dyes. Such complex acids as molybdotungstophosphoric and molybdotungstosilicic were said to be suitable, the former being prepared by boiling a solution containing 90 parts of sodium tungstate and 10 parts of sodium molybdate with sodium phosphate and finally adding hydrochloric acid and a small quantity of nitric acid to precipitate the complex acid¹¹.

Similar acids in presence of complex heteropoly acids derived from gallic or tannic acid were used by Stocks and Linch¹², an example being the formation of a lake from Brilliant Green Crystals YS with mixed tungstophosphoric and molybdodigallic acids. In another process, complex compounds containing titanium have been suggested for lake manufacture, one method of application consisting in precipitation of the dye Rhodamine B by means of titanium molybdotungstate solution, the latter prepared by boiling together in aqueous solution sodium molybdate, sodium tungstate, and titanous chloride¹³. The Cornbrook Chemical Co. have claimed the production of basic dye lakes with complex acids containing selenium dioxide and one or more of the oxides of molybdenum, tungsten, arsenic, antimony, phosphorus, and silicon¹⁴.

Using the leuco compounds of basic or acid triarylmethane dyes as starting materials, Linch, Rodd, and Frew¹⁵ prepared lakes by oxidation in presence of a complex inorganic acid or its components. In one example of the method, leuco Malachite Green in hydrochloric acid solution was oxidised by potassium permanganate containing sodium molybdotungstophosphate. In a closely related process the leuco compounds were treated in absence of oxidants with tungstophosphoric acids, and the precipitates so obtained converted to colour lakes by subsequent oxidation with hydrogen peroxide, ferric hydroxide, etc.¹⁶.

Other improvements produced by varying the conditions under which the lakes were formed included precipitation with solutions of the complex acids or their salts, the pH values of which had been adjusted to between 7 and the pH of the corresponding acid salt¹⁷. Stead has emphasised the importance of pH control in the production of colour lakes of the Fanal (IG) type, and has pointed out that in certain cases the pH at which precipitation is carried out has a marked influence on the tendency of colour to bleed from the lake into certain solvents¹⁸. If, after precipitation, lakes are boiled with water or some other wetting but non-destructive liquid at ordinary or increased pressure, greater light fastness has been said to result¹⁹.

Reduced compounds of phosphomolybdotungstic acid, prepared by treating acids of the general formula $P_2O_5 \cdot aWO_3 \cdot bMoO_3 \cdot 3H_2O$ ($a + b = 18$ or 24) with reducing agents, such as sulphur dioxide, sodium thiosulphate, and glucose, have been claimed to give lakes of much better light fastness than obtainable before²⁰. The use of these compounds for lake formation is believed to be the basis of the Fanal colours. A subsequent patent claimed that lakes of still greater fastness to light were obtained if the aqueous suspensions obtained by precipitation of basic or acid dyes with such reduced heteropoly acids were boiled with water²¹. If the lake were precipitated by the normal complex acid and then treated with reducing agents such as sodium bisulphite and nascent hydrogen, improved fastness resulted²².

A later process²³ for producing reduced complex acids suitable for lake formation from their components covered a much wider range of possible

compounds. It was suggested that soluble derivatives of molybdenum and/or tungsten be mixed in solution with compounds of phosphorus, silicon, iron, chromium, aluminium, arsenic, antimony, boron, or manganese, and the whole treated with a reducing agent such as glucose or sodium dithionite (hydrosulphite). The products were then separated by salting out or by passing hydrochloric acid gas into the aqueous solution.

A number of processes were devised in which a basic dye and some other organic base were precipitated together by complex heteropoly acids. In one I.G. patent, for example, fast-to-light lakes were claimed as a result of treating a basic dye with a complex phosphotungstic acid and an acid dye having at least one amino group and one or more sulpho groups²⁴.

Du Pont, on the other hand, prepared lakes by bringing together in acid solution a basic dye, an aliphatic amine such as tripropylamine or dibutylamine, and a complex acid containing tungsten or molybdenum or both²⁵.

Lakes have been claimed from compounds which are not basic or acid dyes but which contain amino groups, e.g. *p*-aminobenzoic acid, by precipitation with complex phosphomolybdotungstic acids²⁶. The same type of compound could be mixed with a basic or an acid dye containing at least one amino group before precipitation with the complex acid, an olive-green lake being obtained from a mixture of *p*-aminobenzaldehyde and Victoria Pure Blue BO²⁷.

Lakes fast to light, oil, and spirit, and said to be superior to the corresponding lakes from triphenylmethane dyes, have been prepared by treating cyanines, carbocyanines, and related photographic sensitizers with complex acids of tungsten and molybdenum, an example being a yellow lake from 1:3:3:1':3':3'-hexamethylindocyanine chloride (Astra Violet FF) and a complex phosphotungstomolybdic acid²⁸.

The mechanism of the reaction between basic dyes and heteropoly acids is believed by Richards²⁹ to be one of salt formation. The acids are of the general type represented by the dodecatungstophosphoric acid of formula $7H_2O.P_2O_5.24WO_3$ and are all heptabasic. Thus, one mole of Malachite Green would require in theory one-seventh of a mole of phosphotungstic acid, and this is approximately the amount required in practice. Many other basic dyes behave similarly, though there are exceptions such as Setoglaurine, Brilliant Glacier Blue, and Auramine. The last-named requires only about two-thirds of the theoretical quantity of phosphotungstic acid for lake formation.

Linz and Coffey, on the other hand, suggest that the lakes are adsorption complexes rather than definite compounds³⁰. This contention is supported by the researches of Neergaard^{31,32}, who found that up to a certain maximum, light fastness increased in proportion to the amount of heteropoly acid adsorbed by the lake in excess of that calculated as being necessary for salt formation. The adsorbed acid is present on the surface of the colour lake

particles, and fastness to light is therefore proportional to the surface concentration of the acid. Fading of basic dyes on exposure to light is due to photochemical oxidation, and it appears that the adsorbed complex markedly retards this oxidation by preferentially absorbing the light energy which is normally the cause of fading.

Linz and Coffey³⁰ studied the effect on light fastness of precipitating a number of different dyes with phosphotungstic acid, phosphomolybdic acid, and mixtures of these acids in varying proportions. They found that in general the best light fastness was obtained with a mixture containing 10–25 mol. % of phosphomolybdic acid. Richards, on the other hand, while admitting the superiority of lakes made from phosphotungstomolybdic acids over those from the simpler phosphotungstic acids, claimed that a mixed acid does not yield any better results than phosphomolybdic acid alone²⁹.

One of the earliest references to the use of complex acids as mordants in the dyeing of textiles occurs in a paper by Scheurer³³, who observed that a cotton fabric impregnated with sodium silicotungstate and dried would subsequently dye directly with a basic dye. The dyeings were said to be fast to mild soaping, but were rapidly removed by soap at the boil. He noted, however, that washing fastness was better than when the mordant was tungstic acid alone.

Both F. Bayer & Co.⁵ and the B.A.S.F.³⁴ proposed similar processes for the treatment, with complex tungstic acids or their salts, of dyeings of acid dyes containing both sulpho and amino groups to give improved light fastness. Lendle proposed to treat dyeings of basic dyes by an analogous process⁶.

The product Auxamine B was marketed by the I.G. as an agent for the improvement of the light fastness of basic dyeings on conventional mordants such as antimony tannate or Katanol ON (IG). It is a reduced complex acid of molybdenum, tungsten, and phosphorus, and is applied as an aftertreatment of the dyeings³⁵.

A further suggestion was that cloth should first be mordanted with a complex acid and then dyed with a basic dye. The mordant was itself fixed on the fibre by a preliminary mordanting with a wide variety of fixing agents other than tannin, such as phenol, cyclohexanol, certain carbohydrates, or benzidine³⁶. For the production of prints by an I.G. process the cloth was first prepared in the complex acid and the dye printed separately. The dried print was then steamed to complete the fixation³⁷.

The many processes for the fixation of basic colour lakes as pigments on the fibre surface by means of adhesives are rather outside the scope of this paper and will not be considered.

EXPERIMENTAL

Preliminary experiments based on the known processes, no single one of which was a single-bath treatment, showed that they all suffered from one or more defects, the principal faults being as follows—

- (1) Lack of brightness in comparison with acid dyes as applied by the so called urea method
- (2) Inferior colour yield
- (3) Inferior washing fastness
- (4) Poor fastness to rubbing
- (5) Staining of the white ground in prints
- (6) Light fastness, while in certain cases superior to that shown by antimony tannate alone, not sufficiently good for the standard required.

Furthermore, it was desirable to have a single-bath process if at all practicable.

In a series of simple experiments, it was observed that an aqueous solution of the basic dye Victoria Blue R (C.I. 728) was partly though not completely precipitated by an aqueous solution of sodium molybdate of pH 9.5 when added in slight excess. The precipitated colouring matter redissolved either on addition of ethyl alcohol or on dilution with a large volume of water. If acid were added at any stage, sufficient to bring the pH below, say, 5, then complete precipitation took place and dissolution was not achieved by addition of alcohol. These observations suggested that dye and mordant (sodium molybdate) might be applied together to a fabric and precipitated by acidifying. Accordingly a printing paste thickened with locust-bean gum and containing 3% sodium molybdate together with 1% Victoria Blue R in aqueous alcohol solution of 8% alcohol content was applied to a viscose rayon crêpe fabric and dried. On acidification of the print the colour lake was formed, but the resulting shade was disappointing in respect of brightness and light fastness, and the colour yield was poor. Both washing and rubbing fastness were unsatisfactory. That these results were only to be expected was shown when examination of the printed fibres revealed that the major portion of the colouring matter lay on the fibre surface. When another portion of the same print was steamed prior to acidification, a very different result was obtained, the print being bright and of good fastness to light, washing, and rubbing, and here very uniform colour distribution within the fibre was found to have been produced. Acidification was tried out by a variety of methods, with hot and cold acetic acid and hydrochloric acid and also by acid ageing. Apart from cold acetic acid, all of these seemed satisfactory. It was thought that the necessity for souring or acid ageing might be avoided by the addition of an agent such as ammonium thiocyanate to the printing paste, but this ideal proved to be unattainable. In all cases the lake was fully formed before any substantial fibre penetration could take place, and the results were little better than those obtained by acidifying the original unsteamed print.

It was observed that samples of sodium molybdate obtained from different sources at various times tended to give aqueous solutions of varying pH values, and these in turn led to prints showing desirable or undesirable properties according to whether the pH was high or low. It was found convenient at this stage, therefore, to adjust the pH

of the sodium molybdate solution to about 10. The important question of pH will be discussed in more detail later.

When the same technique was used in the application of other basic dyes, the resultant prints, while bright and of much superior fastness to tannin prints, were not up to the standard shown by Victoria Blue R. The teachings of the pioneer workers in the pigment field were therefore applied, attention being turned to sodium phosphomolybdate, and at once good light fastness was obtained with a large number of basic dyes, though some failed to give a good yield. Victoria Blue B (C.I. 729) was notable in this respect, and indeed, no matter which complex salt and printing technique were used, this dye always gave an extremely low yield of rather dull colour and poor light fastness.

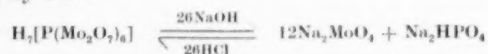
Consideration was given to the use of tungsten compounds in place of molybdenum compounds. Sodium tungstate gave a poorer light fastness than sodium molybdate with Victoria Blue R, and other dyes tested showed analogous inferiority. The complex sodium phosphotungstate gave better results than the simple tungstate but not so good as the phosphomolybdate. Careful comparisons made on a number of dyes between sodium phosphomolybdate alone and mixed with varying proportions of sodium phosphotungstate showed that the pure phosphomolybdate always gave the best results. Even a small amount of the tungsten compound was sufficient to reduce the fastness to a measurable extent. These observations would appear to conflict with many previous claims in the field of pigments, but they do agree with the observations of Richards recorded in more recent times²⁰.

As has been shown earlier, much stress has been laid in the past on the use of the reduction compounds of the heteropoly acids for lake making. Although a great many experiments were carried out with a reduction product of sodium phosphomolybdate, in no instance was a print obtained of superior light fastness to that from the normal sodium phosphomolybdate. Here again, therefore, there would appear to be a difference between the properties of lakes and those of textile prints. It may be, of course, that reduction of the complex acid occurs during steaming at the expense of the printing thickener or even some of the dye itself. This seems unlikely, however, as it was found at another stage that addition of Ludigol (IG) (sodium *m*-nitrobenzenesulphonate) to a number of different printing colours had no adverse effect on the light fastness. Specimens of lakes made with the normal and reduced acids have not been examined in order to verify the claims made in the patent literature, though there is no reason to doubt the validity of these claims, and it may well be that in the case of the complex acids containing both molybdenum and tungsten the results are superior when the complex acid is in its reduced form. This point has not been investigated in prints.

During one stage of the work sodium phosphomolybdate fell into very short supply. Furthermore, it is a very much more expensive material than sodium molybdate, so there were good reasons

why attempts should be made to form the complex acid from its components during some stage of processing, as had been claimed in one of the earlier methods for lake manufacture. This proved to be relatively simple and successful, and it led to some interesting observations and developments. Initially printing pastes were made up to contain 3% sodium molybdate and 0.35% sodium phosphate, and these gave excellent results provided the prints were steamed almost immediately after printing. If there were any appreciable delay, however, colour yields and light fastness tended to be inferior. It so happened that, at the time of this particular stage of the research, the laboratory atmosphere was usually rather acid, and this was believed and finally proved to be the cause. It was therefore decided to use an excess of phosphate, 2 g. disodium hydrogen phosphate per 100 g. printing paste being taken quite arbitrarily, and this change overcame the trouble. The additional phosphate plays no part except to protect the print from contact with acid fumes until after completion of steaming, and it is thus possible to have a time lag of several days or even weeks between printing and steaming. As might be expected, the prints are very sensitive to light fading until the lake has been formed by acid treatment. It is perhaps interesting to note that, prior to this stage, dyes such as Rhodamine B and 6G exhibit strong ultraviolet fluorescence. After souring has precipitated the lakes, fluorescence has disappeared.

The same addition of 2% sodium phosphate as a protective agent to a printing colour containing sodium phosphomolybdate produced results of inferior light fastness with some dyes, thought to be due to the excessive quantity of weak alkali present in the final printing colour. Sodium molybdate is not a strong buffer; i.e. its aqueous solution is readily changed in pH by additions of small amounts of acid or alkali. For its adjustment as previously outlined to a pH of, say, 10.5, only a relatively small addition of caustic soda is usually required. In a typical example, only 0.02 ml. of N. caustic soda per gram of sodium molybdate was sufficient for this purpose. Sodium phosphomolybdate, on the other hand, is a strong buffer, a typical example requiring 1 ml. of N. caustic soda to bring one gram to the same pH value. Thus we have a fairly large amount of potential alkali available. On being heated with excess of alkali, phosphomolybdic acid is broken down into a mixture of sodium phosphate and sodium molybdate, which mixture will recombine in the presence of acid to give the heteropoly acid—



When the additional reactions involving lake formation are considered, the complexity is enormous, and it is not easy to find a definite explanation for the poorer light fastness noted above. It may be that under these conditions a lake is formed with the simple acid in preference to the complex acid. The point was not further investigated, as the difficulty disappeared when the sodium phosphate was replaced by a mixed phosphate buffer of lower alkalinity.

Aqueous solutions of basic dyes vary very much in pH, and their solutions containing sodium phosphomolybdate also vary greatly. Some, which themselves are relatively weak buffers, assume substantially the pH of the mordant solution; while others, which are strong buffers, assume a value approaching that to be expected from neutralisation of an acid with a base. This is illustrated by the examples in Table I. The dyes without mordant were at 1% concentration, and with mordant contained in addition 3% sodium phosphomolybdate. The concentrated mordant when diluted to 3% strength had a pH of 10.5.

TABLE I
pH of Solutions of Basic Dyes

C.I. No.	Dye	Without Mordant	With Mordant
841	Safranine T	7.0	10.5
—	Methylene Blue 2F	1.3	10.5
—	Victoria Pure Blue BO	3.9	10.0
749	Rhodamine B	2.2	6.1
662	Brilliant Green Crystals	2.1	5.8
729	Victoria Blue B	4.8	8.3

By addition of a phosphate buffer these differences in pH can be levelled out somewhat, and this procedure offers some advantages when two or more dyes are mixed before printing. Thus, on addition of a mixed phosphate buffer containing 1.4% sodium hydrogen phosphate and 0.25% sodium dihydrogen phosphate a Brilliant Green Crystals printing colour was found to have a pH of 7.2, and a Victoria Pure Blue BO colour a pH of 9.0. Adjustment of the Brilliant Green to a pH of 9–10 by addition of more alkali led to poor results. It was considered that each dye must be allowed to take up the natural pH produced by itself in presence of the adjusted mordant and the phosphate buffer.

The use of solvents other than water for basic dyes hardly arises in lake manufacture, but in calico printing solvents as printing aids have been the rule rather than the exception. Of these, probably acetic acid and acetin have been most widely used, but other acids, notably lactic and glycolic acids, and also resorcinol have been suggested. In the present process solvents of an acidic nature were automatically ruled out by the findings of the early experiments, and therefore recourse was had to other water-miscible solvents. While such solvents are not essential to the process, and it is perfectly practicable to print many basic dyes which have been dissolved in water only, a small amount of a suitable organic solvent, to dissolve the dye initially, is commonly an advantage. The amounts required need never exceed 1% of the weight of printing paste. Solvents found suitable include the lower aliphatic alcohols, such as methyl, ethyl, and propyl alcohols, the lower aliphatic ketones such as acetone and ethyl methyl ketone, and the glycols and their ethers such as diethylene glycol and β -ethoxyethanol.

The necessity or otherwise for additions of humectants to printing colours depends largely on steaming conditions. For average conditions small amounts of glycerol or urea were found to give improved brightness and colour yields together

with enhanced washing fastness with certain dyes. The maximum amount required is probably not greater than 5%, and this addition contributes some extra solvent power for the dye.

A number of printing thickenings may be used without serious change in the ultimate results. Most of the experimental work was carried out with either carob bean or tragacanth. As might have been expected, carrageen extract was found to be totally unsuitable.

It is perhaps appropriate at this stage to indicate what is meant by "fast to light and washing" in relation to the basic dyes fixed by heteropoly acids. Somewhat arbitrary standards were adopted—S.D.C. No. 3 light test and S.D.C. No. 2 washing test, and in the light of experience these would seem to have been satisfactory. In the foregoing text, therefore, "fast to light" means that the print would pass S.D.C. No. 3 light-fastness test, though it may actually have been appreciably better. Almost all tests were carried out on the C.P.A. fading lamp, though confirmatory tests were made from time to time by daylight exposure.

In a similar manner, washing was considered satisfactory if S.D.C. No. 2 test was passed, though some dyes were capable of passing No. 3 test. Victoria Pure Blue BO, for example, when well fixed reached the latter standard. As might be expected, washing fastness of the pale shades was at least as good as that of the stronger shades, while with light fastness there was the opposite tendency. This, however, need not be serious with proper precautions. With most dyes it was found that, on the basis of 1.5 parts of sodium phosphomolybdate for each part of dye, light fastness fell off sharply with depths much less than 0.5%. By purely empirical means it was found, however, that good light fastness was obtainable provided the concentration of mordant in the printing paste was never allowed to fall below 1%. This clearly fits in with the theories of Neergaard^{31,32}, by suggesting that more phosphomolybdic acid is required than the stoichiometric quantity for salt formation, and that there is some excess of acid adsorbed by the final lakes. That excess acid is not merely deposited within the fibres, independently of the colour lake, is indicated by the fact that cloth printed with a paste free from dye and given normal processing has no greater affinity for a basic dye than the unprinted cloth. Attempts were made to determine the relative amounts of dye and mordant fixed on the cloth under a variety of conditions, and it was found that some excess of mordant over the theoretical amount did in fact obtain. At an early stage, however, it was apparent that very special techniques would have to be devised if accurate comparisons were to be made, and it was not felt that the results to be obtained warranted this departure from the main object of the work.

A very high proportion of basic dyes were found to have good light fastness when applied by the methods outlined, but washing fastness was in many cases not up to the standard of the best. To quote just one example, Brilliant Green Crystals YS (C.I. 662) has excellent light and washing fastness, both appreciably above standard; while Malachite

Green (C.I. 657) is satisfactory to light, but rather poorer to washing. The reason for this marked difference between two such closely related dyes is not easy to understand.

So many basic dyes possess such purity of shade, however, that it is not necessary to have a large number of individual dyes in a range. With a very limited number of bright stock colours, the whole gamut of intermediate tones of equivalent brightness can be obtained by suitable mixtures. The weakest part of the basic dye range is in the yellow-red region, and in general the shades obtainable are much inferior to the best of those to be found in the insoluble azo range. Apart from brightness, basic yellows and oranges rather lack tinctorial power.

The basic dyes were found to be unsatisfactory when printed on a cloth prepared with an azoic coupling component, and the obvious alternative was to use stabilised azoic compositions. Such of the latter as will withstand steaming prior to acid ageing proved satisfactory when printed by a normal recipe. Rapidogen yellows, which of course cannot be steamed when printed with caustic soda in the colour, were applied by the Rapidogen Developer method; the necessary range of colours was thus complete, and the ultimate goal had been reached.

The principal colours would be obtained with basic dyes fixed with phosphomolybdic acid³³, and where a very bright, strong yellow, orange, or red was required stabilised azoic compositions would supplement the range. The fastness to light and the fastness to washing were considered to be fully adequate for normal requirements of dress fabrics, and the colours were found suitable, without loss of light fastness, for permanent finishes, such as crease-resisting and non-shrink finishes, whereby washing fastness was made better still.

* * *

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(MS. received 20th May 1953)

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Discussion

Mr. R. J. HANNAY: The author has stated that attempts to include an acid producing agent in the printing paste proved unsuccessful because lake formation occurred so rapidly that the dyestuff had insufficient time to penetrate into the fibres. Has anything been done with agents which generate acid only gradually, such as, for example, the steam hydrolysable esters?

Dr. W. S. MILLER: In order to get a print which is both bright and fast, the lake must be produced inside the fibre, and to achieve this end neutral steaming of sufficient duration to effect more or less complete absorption must precede acidification. It is true that an ester such as diethyl tartrate develops acid more slowly than a salt such as ammonium thiocyanate, but even so, sufficient acidity for lake formation has been produced before proper dye penetration is achieved. There is additionally some doubt as to whether laking by tartaric acid leads to the best light fastness. This latter property is greatly influenced by the nature of the acid and it can be said that in general the stronger the acid one can use without detriment to the fabric, the better is the result. It must be remembered also that an ester yielding a volatile acid would not be permissible, as excess acid must inevitably mix with the steam and so create the acid steaming conditions which one must be at pains to avoid. The choice of ester is therefore not an easy matter and it can only be said that the use of esters for precipitation of the lake has proved impracticable so far.

Mr. F. CROMPTON: Basic dyes are still used for coloured discharges on dyed grounds. Have any trials been made with the new process in coloured discharges?

Dr. MILLER: Only a few trials have been made with coloured discharges and these were not entirely discouraging. As discharges were subsidiary to the main problem, however, no detailed investigation was made and it would therefore be inappropriate to offer any definite opinion on practicability.

Mr. W. B. MILLER: Has the author any suggestions that the phosphomolybdenum lakes would be of use on cellulose acetate? It is well known that the basic colours can be printed on cellulose acetate without mordant and are then often brighter and faster than the tannin lakes on cellulose.

Dr. MILLER: Attempts to produce phosphomolybdate lakes on cellulose acetate have not been successful and indeed on all non-cellulosic

fibres have proved disappointing. It is true that basic dyestuffs may be printed on cellulose acetate without mordant and show quite marked affinity and it may be this very affinity which limits or even prevents formation of a phosphomolybdate lake. It is suggested that while during steaming the dyestuff is absorbed by the fibre and becomes bonded to the carbonyl grouping as with the amino-azo dyestuffs so largely used for cellulose acetate, the alkali phosphomolybdate remains unabsorbed, with the result that the acidification step does not find dyestuff and mordant in the proper position for lake formation. This suggestion, being unsupported by experimental evidence, is of course purely theoretical. It must be said, however, that when the basic dyes are applied to cellulose acetate by the new method, no appreciable improvement in light fastness is shown, in comparison with the more ordinary method suggested by Mr. Miller. On wool also, improvement in fastness was not obtained when the new method was tried out and it was concluded that the affinity of the wool for basic dyestuffs was too strong to permit the rearrangement necessary to produce the complex phosphomolybdate lake.

Mr. HANNAY: One of the drawbacks to previous attempts to print the molybdophosphoric lakes of basic colours on textile materials was the comparatively poor fastness of the resultant prints to alkaline washing treatments. In view of the rapidly expanding use of alkaline built detergents in the domestic field does the lecturer feel that the method now described gives increased fastness to washing under such circumstances as compared to previous methods?

Dr. MILLER: Previous attempts to print the lakes of basic dyestuffs with complex heteropoly acids were based mainly on acids of tungsten or mixtures of tungsten and molybdenum but not to any extent on molybdenum alone. It is felt that in addition to better light fastness the molybdenum lakes are more alkali resistant. The question of stability is, however, closely bound up with the method of formation of the lake. Much of the earlier work involved fixation of a preformed lake with a binder, and inferior washing fastness was therefore due to a combination of loss of binder and alkaline decomposition of the lake. The standard of washing fastness aimed at was to pass S.D.C. No. 2 test which does not involve an alkaline detergent but at one stage more severe tests with soap and soda were carried out and some dyestuffs showed remarkably good fastness to this treatment.

It can be said that wash fastness even with alkaline washing agents is much better than with older processes, although it should be emphasised that one does not recommend washing fine rayon fabrics with free alkali.

Mr. J. W. RUWNOF: Is it possible to dye viscose rayon by this process and if so, is anything known about the dischargeability?

Dr. MILLER: It is not possible to dye viscose rayon by this process which is essentially an all-in printing method. If the mordant solution be applied in absence of dyestuff and the sequence of process steps carried out, it is found that no

affinity is shown for basic dyestuffs. What has happened, is that no mordant has been fixed, the acidifying conditions being such that an insoluble phosphomolybdic acid is not precipitated in the fibre. What approximates in final result to a dyeing can, of course, be obtained by mangle impregnation with a suitable dyestuff and mordant mixture, and then proceeding as with prints. There are obvious technical objections and difficulties with such a procedure however. As to discharges on padded shades the limited number of trials carried out indicated the same difficulties and disadvantages as with shades dyed on antimony tannate mordant.

Control of Padding Processes by Radioactive Isotope Labelling

H. B. HAMPSON and E. W. JONES

Industrial uses of radioactive isotopes are briefly surveyed. Experiments show that radio-isotope techniques may conveniently be employed to control the regularity of padded cloth, both across its width and throughout its length.

APPLICATIONS OF RADIOACTIVE ISOTOPES

Radioactive materials produced by neutron irradiation in an atomic pile have been available in Great Britain since 1947. They have found applications in many branches of research, in therapy, and in industrial control. This paper deals with their properties and indicates how they may possibly be exploited in textile printing and other processes.

Comparatively few of the possible combinations of protons and neutrons are stable, and if an extra neutron is added to a stable nucleus, say in a pile, the resulting nucleus is frequently unstable. Unstable nuclei are radioactive, since they tend to return to a stable state by emitting α -, β -, or γ -radiation.

The usefulness of a radioactive isotope depends on the following properties —

(i) The atoms are chemically identical with those of the ordinary stable element.

(ii) It emits radiation whose energy is characteristic of the particular isotope. The radiation intensity is attenuated in passing through matter according to definite laws. Most forms of radiation can be detected with a high degree of sensitivity.

(iii) The radioactivity of a given quantity of material dies off exponentially with a half-life which is characteristic of the isotope.

It is also important to know for a particular isotope how much radioactivity can be produced per gram of stable material introduced into the pile.

This depends on a number of factors — neutron-absorption cross-section, flux of neutrons available, and time of irradiation. Table I shows the properties of some pile-produced radio-isotopes.

The radiations can be detected by the ionisation they produce in gases, by their effect on photographic emulsions, or by the scintillations they produce in certain crystals and organic substances. Probably the most commonly used detector is the Geiger counter tube, in which single electrons or β -rays cause current pulses which can be amplified and counted individually. Hence extremely small amounts of radioactive material can be detected.

Safety Considerations

A full discussion of safety considerations in dealing with radioactive materials is outside the scope of this paper, and intending users should consult some authoritative source². In general, the possible hazards can be divided into those due to external radiation exposure and those due to ingestion of the material. In the former case large γ -ray sources are the main consideration, as they may require thick lead screening to cut down the intensity of the penetrating rays. β -Sources can be completely screened by about $\frac{1}{16}$ in. of brass or steel or $\frac{1}{4}$ in. of plastic sheet, etc. The ingestion hazard depends on the chemical nature of the material, which determines how long it will remain in the body. It also depends on the half-life of the

TABLE I
Properties of Radio-isotopes¹

Isotope	Compound	Half-life	Normal Activity (mc./g.)*	Energy of Radiation (Mev.)	
				β	γ
⁷⁶ As	As ₂ O ₃	26.8 hr.	250	3.04, 2.49 1.29	2.15, 1.84 1.25, 0.57
¹³¹ Ba	BaCO ₃	12 days	0.1	None	1.2, 0.5 0.26
⁸² Br	NH ₄ Br ₃	34 hr.	50	0.465	1.35, 0.79 0.55
¹⁴⁰ Cs	BaCO ₃	5700 yr.	†	0.154	None
⁴⁵ Ca	CaCO ₃	180 days	0.07	0.26	None
⁶⁰ Co	Co metal	5.3 yr.	10	0.3	1.3, 1.1
⁶⁴ Cu	Cu metal	12.8 hr.	100	0.58 (—) 0.63 (+)	1.2
⁵⁹ Fe } ⁵⁵ Fe }	Fe metal {	47 days	0.02	0.46, 0.26	1.3, 1.1
		4 yr.	0.02	None	0.0006
¹³¹ I	KI	8 days	†	0.60	0.367, 0.080
³² P	H ₃ PO ₄	14.3 days	†	1.72	None
³⁵ S	Na ₂ SO ₄	87 days	†	0.170	None
¹⁸⁶ W } ¹⁸⁷ W }	W metal {	77 days	2.5	0.69, 0.48	None
		24 hr.	200	1.4, 0.6	0.86, 0.49

* Microrcuries per gram

† Carrier free

isotope. The hazard is greatest in the case of long-lived isotopes which may be built into the permanent bone structure, e.g. calcium 45, radium, and one or two others.

The examples described below will give some idea of the scope of safe applications.

Tracer Techniques

The uses to which radio-isotopes have been put can be divided into general classes. The first class covers tracer techniques, in which the isotope is used as a label in tracing the behaviour of a very much larger quantity of inactive material. In some cases the radioactive material must be used in a form chemically identical with that of the material under investigation. In other cases, it is necessary only that it should be compatible in certain physical properties. Possible tracer experiments in the laboratory or even on pilot-plant or plant scale are legion. Tracers can be used to study distribution of lubricants on fibres, diffusion of ions in solution, effective surface areas of precipitates, efficiency of mixing or separation processes, etc.

In the use of tracer techniques for continuous measurement in industry, i.e. as a form of process control, long-lived radioactivity must not be passed on to the consumer or allowed to contaminate effluents. Unless the tracer can be recovered, a short-lived isotope must be used. Radiophosphorus ^{32}P lends itself to this sort of application, and one or two tracer control problems have been explored with this isotope in Britain. The isotope emits only β -rays, so that shielding problems are small. Very sensitive detection is possible, since the β -energy is sufficient to penetrate the walls of fairly robust Geiger counter tubes. The isotope can be prepared as a soluble phosphate with a fairly high specific activity, so it is suitable for introduction into many chemical processes. Finally, it has a half-life of 14.7 days, which is long enough for shipment and use, but ensures that there is no long-term accumulation of radioactivity in the product or the effluent.

Examples of the application of tracer techniques are the control of colour soiling in the roller printing of textile fabrics³ and the control of padding processes, to be described in detail in the present paper. In these processes, wherever the isotope is present in appreciable quantity it is contained in a large volume of liquid which has self-shielding properties. Owing to the short range of the β -particles, only those originating in the top layer of about 3–4 mm. of liquid can give rise to any external radiation.

The isotope (^{32}P) can be supplied in an aqueous phosphate solution in batches sufficient for about 2–3 weeks' operation of an instrument. A calibrated syringe can be used for dispensing the solution, so that there need be no direct contact with the concentrated material.

Instrument Techniques

In the second class of application, a small long-lived source is incorporated into an instrument, and some property of the manufactured product is measured in terms of absorption or scattering of the

radiation. An example of this is the β -ray "thickness" gauge, which is used to measure continuously the weight per unit area of sheet materials.

Ionisation Techniques

In the third category of applications, the radio-isotope is simply employed to produce ions. Sources have been used to stabilise the striking voltage of spark gaps and discharge tubes, but the most important industrial application in this category is probably the elimination of static electricity. In many industries where insulating materials are processed they acquire electrostatic charges, which make them difficult to handle or cause them to collect unwanted dust. Examples are the combing and weaving of synthetic fibres, the sheeting and folding of plastic films, etc. In many cases a radioactive source can be used to make the air surrounding the material a conductor of electricity, so that the charge leaks away. α -Particles give the most intense ionisation, but in general α -emitters are unsuitable for industrial installation because little or no mechanical protection can be provided for a source without cutting off the α -rays altogether. Pure β -emitters have found most application as static eliminators in this country, and a number are on the market.

CONTROL OF PADDING PROCESSES

An essential condition in padding is that the product used in the padding liquor should be uniformly distributed throughout the whole of the fabric padded. In practice, difficulty may be encountered in maintaining this uniformity for any or all of the following reasons—

- (i) Incorrect strength of the liquor
- (ii) Irregular concentration of the liquor due to inefficient mixing or uneven dilution
- (iii) Variation in mangle pressure across the width due to uneven set or worn rollers.

Where only a fine margin of error is permissible, it is often difficult or impossible to detect variation by the normal methods, which in any case are usually slow and cumbersome—

- (a) Checking the state of the mangle by tests of the uplift at different places across the width
- (b) Testing the cloth at different places in the piece for chemical content per unit area
- (c) Analysis of the padding liquor itself.

It is obvious that by these methods it is not possible to maintain a continuous control on the process, as they are rather protracted, especially those involving analysis. It is therefore not possible to maintain production and to exercise control at the same time.

A second disadvantage of the spot check system is that there is no guarantee that the material between the checks remains correct. The experimental work that has been conducted with radioactive isotope labelling tends rather to indicate that at times it does not so remain.

The series of experiments, initiated with the object of developing a system of continuous control, were grouped as follows—

- (a) Method of labelling
- (b) Correlation between strength of resist salt solution and concentration of isotope
- (c) Setting of instrument
- (d) Trial run
- (e) Bulk running and observations
- (f) Conclusions drawn from the experiments
- (g) Application to resin padding.

A solution of resist salt containing 2 oz./gal. was made, and portions of it were labelled by adding to them radiophosphorus (^{32}P) in proportions varying from 1 microcurie ($\mu\text{c.}$) up to 80 $\mu\text{c.}$ per quart of liquor. Samples of a viscose rayon staple fabric (Utility Specification 1005⁴) were padded through these liquors with a mangle uplift of 80% on the weight of the cloth. A Geiger counter was arranged so that the cloth could then be passed within $\frac{1}{2}$ in. of the sensitive detector.

It would appear from the results (Table II) that labelling of the resist salt pad liquor could be successfully carried out, and satisfactory readings obtained, which would enable continuous control of the padding process to be achieved. The readings in Table II indicate that a concentration of

Degree of Radioactivity ($\mu\text{c.}/\text{quart}$)	Readings
1	Detectable, but partly obscured by background
5	Clearly defined at approx. $\frac{1}{4}$ of the available scale
10	$\frac{1}{2}$ of the available scale
> 20	Off the scale

7.5 $\mu\text{c.}$ per quart would probably be the most suitable. Since the resist salt solution is at a strength of 2 oz./gal., this is equivalent to 15 $\mu\text{c.}$ per ounce of resist salt.

At this strength, and with a mangle uplift of approx. 80%, it would seem probable that, if a Geiger counter of the same sensitivity as that used for the foregoing trials were fitted so that the padded and dried cloth could pass over the detector, and within $\frac{1}{2}$ in. of it, the readings obtained would be conveniently distributed over the scale, and the sensitivity would be of such an order as to indicate very small variations in the strength of the resist salt per unit area of the cloth.

An instrument of such a type as to fulfil these conditions was therefore constructed. It consisted of a Geiger counter the glass of which was protected by a perforated shield consisting of highly polished, smooth chromium-plated iron. In this shield an open window was so arranged that, when cloth was passed over the detector, and touching the shield, the cloth passed within $\frac{1}{4}$ in. of the glass of the detector.

The counter was connected to a meter showing graduations of 0–100, which was so devised that it could indicate the signals from two Geiger counters if necessary, so that both edges of the cloth could be tested during running without the necessity of moving any part of the apparatus.

The instrument is described in more detail in the Appendix.

Fabrics of various qualities were padded in resist salt (2 oz./gal.), labelled with phosphorus 32 at a strength of 15 $\mu\text{c.}$ per ounce of resist salt, and the padded and dried cloth was passed over the counter in contact with the smooth shield.

It was found that in some cases of heavy and absorbent cloths the readings were very high, and it was considered advisable to repeat the experiments with a radioactivity strength of 7.5 $\mu\text{c.}$ per ounce of resist salt. The readings at this strength were found to be very conveniently placed on the scale, i.e. the lighter cloths gave readings of the order of 25, whereas the heavier ones gave readings of 60–80.

An instrument was then fitted at the take-off end of a stenter on which fabric was being padded with resist salt in bulk. This instrument consisted of two Geiger counters attached to a meter in such a manner that the signals from each counter could be indicated independently. The arrangement was used to check bulk running of cloth prepared with resist salt, the impregnation liquor being labelled with phosphorus 32 at 7.5 $\mu\text{c.}$ per ounce of resist salt.

The results are shown in Tables III and IV.

The most significant feature of these results is the close relationship of the two counters and the substantial variation between individual lumps or pieces of the same quality of the viscose rayon staple fabrics (Table III).

It has been observed that, in discharge printing particularly, there is a tendency for outlines and fine work to show variation in mark as between different lumps of staple-fibre fabrics. In the majority of cases it has not been possible when this has occurred to detect by analysis any corresponding variation in cloth construction, or in resist salt content, which would account for such variation. In other words, the printing machine is acting in these cases as a highly sensitive indicator. It now appears that the padding monitor acts in a similar way, and with an even greater sensitivity.

In certain cases (marked with an asterisk (*)) a wide variation was shown between some lumps and others, in a single run through the same liquor. The changes took place sharply at the piece-ends. No detectable differences could be found in cloth structure or quality, but in a proportion of these cases differences in absorbency as shown by sinking tests on the yarn indicated a tendency to a higher absorbency when the figures shown by the meter were higher.

As regards Table IV, consistent results were obtained on all fabrics, so far observed, other than those of viscose rayon staple fibre.

It is of interest to note that on one occasion there was an unexplained fall in the readings (marked with a dagger (†)), which on that fabric had been very consistent. The liquor remaining in the box was found to be low in strength. A thorough examination of the equipment revealed that the steam coil in the mixing tank contained a hole, which made it in effect an open-ended pipe. At certain times of the day the steam was liable to carry an undue amount of water, and this in conjunction with the fact that the liquor level was

TABLE III
 Viscose Rayon Cloths

Date	Fibre	Cloth Description	Strength of Resist Salt			Time	Geiger Reading	No. of Counters	Pieces No.	Way No.
			Weight (oz./sq.yd.)	Prepare (oz./gal.)	Label (μ c./gal.)					
6 Oct. '52	Staple	Utility 1005	4.5	1.5	22.5	11.00 a.m.	Off scale	One		
6 Oct. '52	Staple	Utility 1023	6.95	1.5	22.5	11.30 a.m.	Off scale	One		
6 Oct. '52	Staple	Utility 1023	6.95	1.5	17.0	2.15 p.m.	98	One		
7 Oct. '52	Staple	Utility 1023	6.95	1.5	11.25	3.40 p.m.	28	One		
						4.00	46			
						4.30	46			
						5.05	46			
8 Oct. '52	Staple	Utility 1023	6.95	1.5	11.25	9.10 a.m.	39	One		
						9.45	37, 38		195 (New mix)	
							38, 36, 40		197	
							38, 36		199	
							41, 42, 44		184	
							44		185	
							44, 40		196	
							40, 42		201	
						10.30	41, 42		198	
10 Oct. '52	Staple	Utility 1040	4.85	1.5	11.25	10.50 a.m.	20	One		
							Off- Gearing side			
2 Dec. '52	Staple	Non-utility	3.75	1.5	11.25	10.00 a.m.	50 60	Two		
						10.10	68 68			
						10.20	48 50			
						10.30	60 62			
						10.40	36 38			
						10.50	38 40			
						11.00	44 46			
						11.10	46 46			
11 Dec. '52	Staple-filament	Non-utility	5.25	1	7.5	10.40 a.m.	28 30*	Two		
						10.50	40 40			
						11.00	32 34			
						11.10	40 42			
						11.15	24 20*		15	1
						11.16	36 40		6	1
						11.20	36 40			
						11.22	26 28		3	1
						11.25	40 38		11	1
						11.28	16 20*		5	1
						11.29	42 46		20	1
						11.34	12 12		17	1
						11.35	34 36		17	1
						11.37	18 12*		9	1
						11.38	40 37		1	1
						11.38	46 46		1	1
						12.07 p.m.	38 36			2
11 Dec. '52	Staple	Utility 1040	4.85	1.5	3.7	1.30 p.m.	Off scale	Two	Irregular cloth. Big variation from lump to lump	
						1.45	Off scale			
						1.46	20 22*			
						1.48	12 10*			
						1.58	82 88			
						1.59	40 40			
						2.10	Off scale *			
						2.15	0 10*			
						2.17	92 88			
						2.35	Off scale *			
						2.40	64 70			
						2.44	60 64			
						2.46	Off scale			
14 Jan. '53	Staple	Utility 1009	5.3	1.5	11.25	11.05 a.m.	46 44	Two		
						11.10	50 46			
						11.15	60 46			
						11.20	70 50			
						11.25	70 70			
						11.30	62 60			
						11.35	66 64			
						11.40	76 74			
						11.45	66 64			
						11.50	62 62			
						11.55	66 66			
						12.00 p.m.	72 72			
						12.05	70 70			
						12.10	70 70			

TABLE IV
Rayon and Cotton Cloths

Date	Fibre	Cloth Description	Weight (oz./sq.yd.)	Strength of Resist Salt Prepare (oz./gal.)	Label (μ c./gal.)	Time	Geiger Reading	No. of Counters	Remarks
6 Oct. '52	Viscose rayon fine filament	Marocain	3.31	1	7.5	2.15 p.m.	20	One	Consistent readings through run
8 Oct. '52	Viscose rayon fine filament	Marocain	3.15	2	15	10.45 a.m.	34 36 34 36 40 38 34 3.30 4.00	One	Consistent low readings of 26-29
						3.20 p.m.	29		
						4.30	34		
						5.30	36		
9 Oct. '52	Viscose rayon fine filament	Marocain	3.15	2	15	9.00 a.m.	38 40	One	Consistent readings through 2600 yd.
1 Dec. '52	Viscose-cupr- ammonium rayon fine filament	Taffeta	2.54	2	15	1.20 p.m. 2.45	25 25	One	Consistent readings through 2000 yd.
2 Dec. '52	Cotton		3.07	2	15	2.30 p.m. 2.40 2.50	50 46 52	Two	Both edges and approx. 8 in. in from edges indicated
							52 54		
3 Dec. '52	Viscose rayon fine filament	Crêpe	2.54	2	15	2.00 p.m. 2.10 2.20 2.40 2.50 3.00 3.10 3.20 3.30 3.40 3.50 4.00	40 36 38 34 44 46 37 34 38 34 38 37	Two	
7 Dec. '52	Viscose rayon fine filament	Marocain	3.2	2	15	10.00 a.m. 10.10 10.20 10.30 10.40	36 40 38 40 36	Two	
11 Dec. '52	Cotton		3.95	2	15	3.10 p.m. 3.20 3.30 3.40 3.50 4.00 4.20 4.25	82 84 70 76 86 68 80 84	Two	
29 Jan. '53	Cotton		3.15	2	15	9.45 a.m. 9.50 9.55 10.00 10.05 10.10 10.15 10.20 10.25 10.30	38 34 34 35 32 32 34 32 34 34	Two	

TABLE IV—continued

Date	Fibre	Cloth Description	Weight (oz./sq.yd.)	Strength of Resist Salt Prepare (oz./gal.)	Label (μ c./gal.)	Time	Geiger Reading	No. of Counters
12 Jan. '53	Viscose rayon fine filament	Crêpe	3.0	1	7.5	10.00 a.m.	26	One
						10.05	30	
						10.10	30	
						10.15	30	
						10.20	32	
						10.25	28	
						10.30	28	
						10.35	26	
						10.45	30	
						10.55	28	
						11.00	30	
						11.15	26	
						11.25	28	
						11.30	28	
						11.35	28	
						11.40	26	
						11.50	28	
						12.00 p.m.	30	
						12.05	30	
						1.20	26	
						1.30	26	
						1.40	24	
						1.50	28	
						2.00	24	
						2.10	24	
						2.20	26	
						2.30	30	
21 Jan. '53	Cotton		3.15	2	15	11.05 a.m.	32 27	Two
						11.10	28 23	
						11.15	35 32	
						11.20	35 32	
						11.25	35 32	
						11.30	35 32	
						11.35	34 28	
						11.40	34 30	
						11.45	34 32	
						11.50	33 33	
						11.55	34 33	
						12.00 p.m.	34 32	
13 Feb. '53	Cotton		3.15	1.5	11.25	10.20 a.m.	30 32	Two
						10.25	32 32	
						10.30	33 30	
						10.35	38 36	
						10.40	40 38	
						10.45	40 39	
						10.50	40 38	
						10.55	42 38	
						11.00	40 40	
						11.05	39 40	
20 Feb. '53	Cotton		3.15	2	15	11.00 a.m.	38 34	Two
						11.05	40 40	
						11.10	44 44	

low had severely diluted the padding liquor. These goods were corrected before printing, and it is reasonable to say that by no other means would such a fault have been detected before actually printing the fabric.

CONCLUSIONS

(1) Consistency of padded cloth throughout a run, and from place to place within the piece, can be accurately checked by means of the monitor during running, if so required.

(2) This is of particular value in processes such as resist salt padding, where corrections can be made before the cloth is printed, as opposed to the more common practice of finding out after printing, when it is too late.

(3) It can also be valuable for the control of synthetic-resin impregnations. Consistent resin

content can be assured thereby during actual running at any time before washing. Observations on this aspect of the process are still being carried out.

(4) Variations in absorbency of viscose staple fabrics are clearly indicated by the instrument.

The implications of these differences are still the subject of investigation, but they would appear to be related to similar variations which appear at times without warning in certain types of printed patterns on similar cloths.

Appendix

PADDING MONITOR

Two instruments are used for this purpose. The first (Fig. 1) is a "labelling" meter for checking the liquid to ensure that the correct amount of radioactivity is associated with a given weight of the

material to be applied to the cloth. This consists of a Geiger counter which can be immersed in the liquid. It has a special watertight housing to protect the electrical connections, and is connected by a short cable to a small portable battery-operated meter which has a fixed mark on the meter scale corresponding to the correct labelling strength.

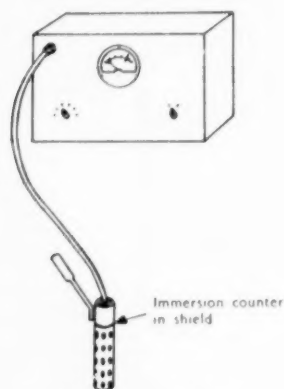


FIG. 1—Labelling Meter

The second instrument (Fig. 2) is the padding monitor itself, and is mounted in a convenient position such that the padded and dried cloth can be passed across the exposed counter glass. It operates from the mains electricity supply. There are two thin-walled β -counters, each about 4½ in. long, mounted at a fixed distance (¾–2 in.) from the cloth, and lying parallel to its width. They are connected by cables to a rate-meter unit, which also contains the high-tension voltage-stabiliser circuit. In the rate-meter the Geiger pulses are integrated continuously to give a current proportional to the number of pulses per second. There is a single meter scale, and the instrument is provided with a selector switch so that the signal from either one of the Geiger counters can be displayed on the meter.

Dr. W. SHAW: No mention is made in the paper of the exact relationship existing between the liquor uptake of the padded fabric and the Geiger counter readings observed, while an inspection of the figure quoted in Tables III and IV does not support the view that the connection is one of simple proportion. It is consequently not possible to assess the true magnitude of the padding variations occurring from the recorded figures. Could the lecturers therefore state how the liquor uplift of the cloth is determined from the counter readings, and what is the significance in terms of change in cloth resist salt content of the variations observed, for example, when padding Utility 1009 cloth on 14th January 1953. (Table III.)

Mr. H. B. HAMPSON: The relation between indicator reading and tracer concentration in the cloth is very approximately linear. The zero of the meter scale does not correspond to zero concentration, however.

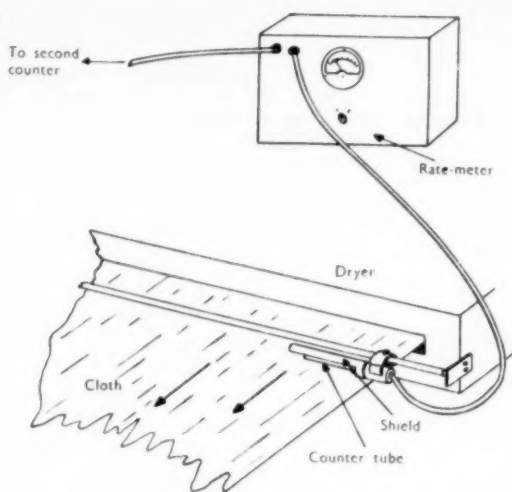


FIG. 2—Padding Monitor

Variations across the width of the cloth can be studied by mounting one counter at each edge, and switching from one to the other, or by scanning a single counter slowly across the web.

ISOTOPE DEVELOPMENTS LTD.
BEENHAM GRANGE
ALDERMASTON WHARF
NEAR READING
BERKSHIRE
UNITED TURKEY RED CO. LTD.
ALEXANDRIA
SCOTLAND

(MS. received 4th March 1953)

References

- ¹ Complete lists obtainable from Isotope Information Office, A.E.R.E., Harwell, near Didcot, Berks.
- ² Medical Research Council, *Introductory Manual on the Control of Health Hazards from Radioactive Materials* (London: H.M.S.O.).
- ³ Meitner and Hampson, J.S.D.C., 69, 283 (Aug. 1953).
- ⁴ *Utility Apparel Cloth—Cotton, Rayon, and Linen* (Schedule NW 2. H.M.S.O., 1947), Section II—Rayon Cloths.

Discussion

Any proportion of the detector signal can be "backed off" including the natural background signal of the Geiger counter.

The scale used for Tables III and IV is a purely arbitrary one, chosen for convenience, and represents only a proportion of the total content.

It is possible to relate the readings to the content of "labelled" substance per unit area of cloth, but owing to the great number of variations due to differences in absorbency, in mangle uplift in changing qualities of fabric, this would necessitate a separate calibration for every quality. The arbitrary scale was selected therefore to avoid this complication. It embraces all fabrics likely to be encountered, and registers, very accurately, and instantaneously, any departure from regularity either across the width of the fabric or throughout its length.

The amount of tolerance allowable depends upon

the nature of the work and the individual user's own requirements.

In Table III, Utility No. 1009, on 14th January, it is seen that there are low readings during the first 10 minutes of running. This lag when the instrument is first switched on at the beginning of a run has been observed on several occasions and the cause is as yet in some doubt. It has been the practice to ignore the preliminary readings on this account and use those observed after the instrument has "settled down".

In this particular run the readings vary, in the case of the off side counter, between 60° and 76° over a run of 55 minutes. The gearing side counter is registering between 60° and 74° over a period of 45 minutes. After the "settling down" period, the two counters are registering independently almost identical readings. Readings are taken in all cases on separate lumps, so that the instrument in this case is showing slight variation between lump and lump, and complete regularity from edge to edge. The lengthwise variations shown in this case are very small (less than 5% in total content) and the padding regularity is satisfactory.

Dr. SHAW: When dyes or other substances, having an affinity for the fabric, are applied by a padding process, it is well known that the concentration resulting in the padded fabric can differ from that of a non-substantive substance applied under similar circumstances. A tracer such as sodium phosphate would therefore appear to be of little value in this instance. Has any means been found of overcoming this difficulty?

Mr. HAMPSON: The system is not applicable to substances with a pronounced affinity for the fabric.

Mr. B. C. VAN NOORDWIJK: How many counts per minute correspond with scale value of 100? This in respect to the background that is always present in Geiger counters.

Mr. JONES: A typical value of sensitivity would correspond to 600 counts per minute for full scale deflection. The background is dealt with in practice by a simple tuning device.

Mr. VAN NOORDWIJK: Is it possible to make the dye itself radio active. That would overcome any difficulty as to whether the indicator is really indicative of the amount of dye.

Mr. JONES: It would be possible in some cases to incorporate a radio-active atom into the dye-stuff molecule. In practice, however, there would be great difficulties in the way of such a system, because of necessary safety factors with a dry dyestuff, and the problem of selecting an isotope which would leave the dyestuff properties undisturbed, and yet have a sufficiently long half-life to give good storage properties.

Mr. VAN NOORDWIJK: Can you give an idea as to the cost of isotopes, e.g. £c per millicurie?

Mr. JONES: The cost of isotopes produced in the pile depends upon the neutron flux available at the time of irradiation. Details can be obtained from The Isotope Division, A.E.R.E., Harwell, Berks.

Mr. F. SMITH: Had the author finished out a piece of fabric with a variation of 12 to 80 to ascertain whether or not any fault was apparent, as 12-80, according to Mr. Hampson, only represents a minimum difference of 5 per cent. and according to Ellis (*Measurement of Colour by Photo-electric Principles*) the human eye cannot detect differences up to 6 per cent.

What is the maximum difference in the reading allowable before making any correction?

Mr. HAMPSON: The scope of the scale 0°-100° may be suited to user's requirements according to the work in hand.

The degree of sensitivity used in the work under review is convenient for the class of fabric and the nature of the work concerned.

The amount of tolerance indicated as allowable to a charge-hand would be in the case of resist salt padding be governed by two factors—the nature of the fabric, and the character of the pattern to be printed.

Fine work in discharge designs is sensitive to vagaries in resist salt content in the cloth, and would call for a smaller degree of tolerance than would heavier and more solid patterns.

In the case of fine work, a tolerance of between 30°-70° would probably be the limit whereas with heavier patterns it might be sufficient to use the whole scale.

Variations between the two counters, i.e. between one edge of the cloth and the other, or between sides and middle would be allowed less latitude because in this case differences show a probable maladjustment of the mangle or unevenness in the bole.

Dr. T. VICKERSTAFF: I would like to ask the lecturers what are the real advantages of the radio-active tracer method over the alternative systems which might be used. The radio-active method encounters difficulties whenever substantive compounds are being applied and there is also the difficulty of a supply of fresh isotopic material and variability of radio-activity. A record of the moisture uptake of fabric in padding might be obtained by dielectric measurements immediately after the nip. Another possibility is the use of photoelectric methods using either the light absorption properties of the compound itself (visible or U.V.) or alternatively the use of a Fluorescent indicator which could be detected and measured at any stage by a suitable U.V. illuminator and photoelectric cell.

Mr. HAMPSON: The chief advantages of the radio-active tracer method are accuracy and simplicity.

The only responsibility of the actual user, that is to say the man in charge of the machine, is to watch an indicator dial, and if the needle strays outside the tolerance limits given to him to report the fact.

The method is not suitable for products which are highly substantive, but can be used for those of low substantivity as for example some of the naphthols.

The question of supply of isotope material has so far offered no difficulty. The "label" is supplied by post at pre-arranged intervals, marked with its date of origin, and strength in millicuries at that date.

The addition of isotope "label" is preferably carried out by a laboratory assistant who is supplied with a graph showing the fractions of initial activity plotted against the decay time in days (see Fig. 3).

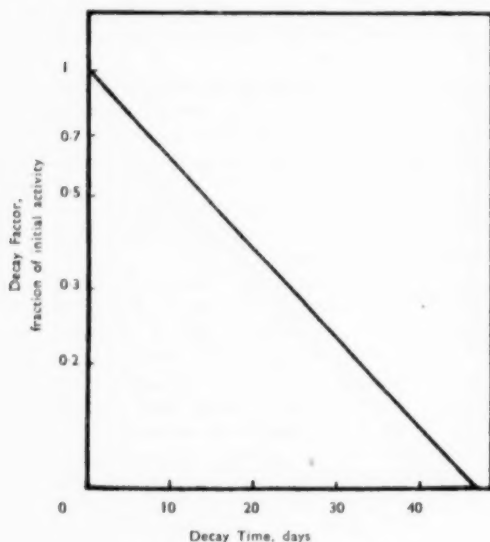


FIG. 3—Decay Chart for ^{32}P Label

The rate of decay is exact, and the final activity in the "labelled" liquor is therefore constant.

The dielectric method is rather insensitive and the necessity to use it immediately behind the mangle gives rise to inconsistency in readings.

It is understood that this has been tried and abandoned for this reason.

We have no experience of photoelectric methods for this purpose.

It would seem possible that a fluorescent tracer may suffer from interference due to fluorescence in the padding liquor, if some of its constituents happened themselves to possess fluorescent properties.

Mr. H. S. POGSON: In padding processes involving direct dyes, Indigosols, and naphtholates, reduction in the concentration of the padding bath occurs owing to substantivity. The radioactive isotope is non-substantive, and will remain constant in concentration, while the concentration of the material padded will inevitably fall, the isotope being no longer an indicator of concentration.

Is the use of a radio-active isotope impracticable in these instances?

Mr. HAMPSON: The isotope tracer technique is not suitable nor is it intended, for materials of high substantivity.

It may be applied, however, if the substantivity is low enough to allow of a normal padding process.

By a normal process is meant padding through a full-sized impregnation box (say of 30–40 gallons capacity) with no special precautions against exhaustion.

Thus it is applicable to certain naphthols, if a fine degree of regularity is required.

Such naphthols of low substantivity are Naphtol AS, AS-D, and AS-OL.

High substantivity naphthols, for example Naphtol AS-SG, AS-SR, AS-SW would not normally be applied by such a padding process and the isotope "labelling" technique would not be suitable.

Mr. J. F. MASTERS*: Fig. 2 shows the counter-tube in position. This projects only a few inches in from the selvedge. How, then, is the distribution of the dye recorded in the centre area of the cloth?

Mr. HAMPSON*: The checking of the fabric across its whole width can be accomplished by mounting the two counters so that one scans the centre of the piece and the other one of the edges.

This latter counter may be moved alternately to either edge.

Alternatively one counter may be mounted to move across the width as mentioned in the paper.

Another method is to mount a third counter, and plug it in alternately with one of the other two.

Mr. N. B. KATRAK*: Can the cloth be sold without washing when this method of "labelling" is used to control the padding of finishing solutions?

Mr. HAMPSON*: The actual amount of radio activity left in the fabric after "labelling" is extremely small, and does not constitute a health hazard.

In addition, the half-life of ^{32}P being $14\frac{1}{2}$ days, ensures that even this small residual amount has virtually disappeared by the time the goods are in the hand of the ultimate user.

Mr. KATRAK*: Can this method of "labelling" be used to control naphthol padding? If so, what radio-active isotope will be best suited for naphthol padding and what will be its approximate cost per 100 gallons of naphthol solution?

Mr. HAMPSON*: If it is desired to "label" certain naphthols, the most suitable isotope would be phosphorus 32. The amount of ^{32}P in one gallon of "labelled" naphthol solution would be the equivalent of approximately 11 microcuries.

The cost of this could be obtained by applying to The Isotope Division, A.E.R.E., Harwell, Berks.

* Communicated

The Printing Efficiency of Vat Dyes

A. G. H. MICHIE and R. THORNTON

A method of assessing vat-dye prints has been established involving determination of the amount of dye applied to a cotton fabric by a roller printing technique, and the amount fixed at various stages during the afterprinting processes. By extracting the vat dye from the fabric and determining optically the amount present in a given area it is possible to calculate the percentage dye fixation under a variety of conditions.

This method of assessment was used initially to study a range of seventeen vat dyes, applied by the potassium carbonate-Formosul process under conditions of varying Formosul concentration in the print paste, varying steaming times, and varying depths of shade. Later the effect of using different alkalis at various concentrations was studied, and also the effect of the addition of glycerol and of different thickening agents.

The predominant feature which emerged was the marked difference between the dyes in sensitivity to the Formosul concentration in the print paste. The dyes varied from those showing little change in percentage fixation, despite large variations in the amount of Formosul present, to those requiring a "threshold" concentration for adequate fixation, while a final group showed the threshold effect and was also susceptible to over-reduction at still higher concentrations. It is apparent, therefore, that the instability of Formosul gives rise to the bulk of troubles experienced in printing vat dyes, since, provided the required amount of Formosul was added to the print paste and remained on the print up to the time of steaming, all vat dyes could be satisfactorily printed.

Varying the thickening agent did not affect the amount of print paste applied to the fabric nor the percentage dye fixation, though marked visual differences were apparent. Caustic soda was shown to be a more efficient alkali than potassium or sodium carbonate, giving both increased percentage fixation and increased rate of fixation. The addition of glycerol had the greatest effect when the steaming times were short.

A preliminary study of the pad-steam process showed a general decrease in the sensitivity of the dyes to the amount of Formosul present on the prints. The basic underlying principles were the same, however, since the order of "printability" was the same for both the pad-steam and the potassium carbonate-Formosul process.

Introduction

The overall high fastness properties of even the earliest vat dyes coupled with their tinctorial appeal immediately stimulated intense interest amongst textile printers, in spite of the obvious technical problems which attended the application of such dyes. Throughout the past thirty years this interest has been not only maintained but intensified and developed in many diverse ways, and has involved extensive investigation and research throughout the industries concerned.

Evidence of the difficulties confronting the vat dyer and the vat printer was the interest aroused by the introduction of solubilised vat dyes, and the present-day widespread use of pigment printing compositions for certain styles of printed goods is undoubtedly the joint outcome of the discovery of phthalocyanine pigments and the wish to avoid the technical hazards associated with the successful production of vat-dye prints at high rates of production.

Despite many discouragements, progress by research workers, dye-manufacturers, textile printers, and textile machinery engineers has never faltered, vat dyes continue to be used in ever increasing amounts for printing, and it can be said to-day that, "for those who will", vat dyes, processes, and equipment exist whereby a printed fabric of outstanding beauty and durability may be made available at a reasonable cost.

The processes used for printing vat dyes can be conveniently subdivided into those in which the reducing agent and the alkali are present in the printing paste and those in which the printed fabric is subsequently padded in a solution containing alkali and reducing agent. The latter technique has recently aroused great interest in the U.S.A., but this is by no means a novel approach. As early as

the late 1920s various processes based on the application of vat dyes with methyl cellulose as the thickening agent were put forward by the former German I.G. Farbenindustrie AG.¹ but, as recommended, these proposals were not very successful and were never really adopted on any major scale. About the same time, also, the use of the British festoon continuous steamer, with its freedom from roller troubles and an easily attained steaming time of twenty minutes, was being recognised as an excellent piece of equipment for steaming vat dyes. It needed only the IG process and the festoon steamer to come together under the auspices of the experienced British vat printer for a pad-steam method to be evolved which has been running most successfully and on an ever increasing scale for the past twenty years. The process has its problems, primarily mechanical at the padding mangle, where the preservation of the printed mark is troublesome; but the difficulties associated with Formosul degradation during drying and on storage of the prints, coupled with the problem of controlling the temperature rise in the steamer normally experienced in the conventional vat-printing method, all disappear with this process, as the goods are steamed wet and no Formosul is used during the actual printing operation. The methods now receiving much attention in the U.S.A. have more in common with the original proposals, in that they employ caustic soda and sodium hydrosulphite, and very short steaming periods—normally less than one minute.

The work which has so far been published on the problems associated with the printing of vat dyes consists in the main of historical reviews contributing little to the understanding of the fundamentals underlying the processes involved. Therefore, the authors' object has been, while accepting that adequate printing techniques do exist, to

attempt a scientific explanation of such techniques based on carefully designed laboratory experiments.

Other scientific workers have recognised the paucity of published findings, and the papers of Meggy², Glarum³, Marshall and Peters⁴, Fordemwalt and coworkers⁵, Turner and co-workers⁶, Sumner, Vickerstaff and Waters⁷, etc. are all very real contributions to the fundamental study of vat printing as distinct from reviews of technology.

In spite of the varied approaches used by these workers, it is noteworthy that sooner or later the investigator, faced with the fact that textile printing involves several distinct operations, all of which are important and may influence the final result, is forced into attempting to single out one particular operation for study. Difficulty then arises in interpreting the results of such work, because the individual operations forming the total printing process are to some extent interdependent.

In our experiments many tedious controls have had to be devised and introduced in order to obtain reproducible results, and novel methods of print strength estimation by optical means have also had to be developed. Once reliance could be placed on these quantitative assessments of yield, the work of examining the vat printing processes under standard conditions became immensely simplified.

Scope of Present Investigation

The assessment of the prints throughout this work has not been carried out visually but by extracting the dye present on the prints at various stages and estimating optically the amount of dye present in a given area. The amount actually printed on the fabric in the machine having been estimated, it is then possible to calculate the percentage dye fixation at any stage of the process. On expressing the results graphically, the effect of print paste variations is shown up more clearly than by the conventional visual assessments. In practice close agreement was obtained between the percentage fixation measurements and visual assessment of the prints except when changes in the thickening agent were made.

It is impossible to cover in one paper the application of all vat dyes by all known techniques to all fibres, so the present work has been confined to mercerised cotton and to selected dyes. It is proposed at a later date to extend the scope of the investigation to include other fibres such as unmercerised cotton, viscose rayon—in particular viscose rayon staple—and half-bleached linen.

The effects of the following variations in the conventional vat-dye printing processes have been studied—

(i) Variations in the formulation of a conventional alkali-sodium formaldehyde-sulphoxylate* printing paste for a range of selected vat dyes generally accepted to represent excellent, moderate, and poor printing properties. The processing operations of printing, drying, steaming, oxidising, and wet-aftertreating have been rigidly controlled to establish optimum standards.

(ii) Variations in the printing gums used for any one vat dye, the other variants in the printing paste being maintained at or around known optima.

(iii) Variations similar to those given under (i) but using a pad-steam development technique and a locust-bean gum as printing medium.

(iv) Finally an assessment has been made of the losses on a multicolour roller printing machine due to "crushing". These losses arise because the impression made on the fabric by the first printing roller is subjected to the pressure of the unengraved portions of the second and subsequent printing rollers, and the print paste applied by the first roller is forced more completely into the cloth, part being removed on the surface of these later rollers.

Experimental

1. PRINTING OPERATION

The printing of the patterns has been carried out in the main on laboratory hand printing machines. Considerable experience is required with these small machines with regard to the type of engraving, the setting of the doctor, and the use of correct pressures for any given blanket and back-grey before reliable, reproducible results can be obtained, but this is only a question of operating experience.

For this work a mill-engraved striped roller was used, and a mark was made on the roller so that patterns could be selected which had been made by the same portion of the engraving. The same stripe was used for printing a series of patterns, and the pressure on the machine was unchanged during the preparation of the prints. This attention to specific detail is essential for reliable results.

2. PROCESSING

Apart from ageing, the finishing processes have been rigidly standardised for each series of experiments, this being relatively simple. To standardise ager conditions is more difficult. The ager employed was of the Mather & Platt roller type, the patterns being pinned on a back-grey, then quickly run into the ager, and kept stationary during the period of ageing. Before the work was begun, a careful study was made of the fixation obtained throughout the ager. The results were surprisingly consistent, but by using certain fixed central positions in the ager the variations arising during the ageing process were further limited. A check was introduced by steaming a standard control print of 7.5% Caledon Printing Red 3B 200 paste with each series of experiments and measuring the percentage fixation. This print was deliberately made sensitive to steaming conditions by printing with 8% Formosul instead of the 12% normally required, and in practice the percentage fixation was found to vary within $\pm 3\%$. The series of experiments for each dye were arranged so that check points were obtained where the printing and fixation conditions were identical. This again ensured that no serious discrepancies arose between experiments.

3. DYE ESTIMATION—METHOD OF EXTRACTION

The patterns for extraction and estimation of both fixed and unfixed prints were obtained by punching out standard areas by means of cutting dies. The position of the patterns was controlled by

*Hereafter called by the trade name "Formosul" (Br).

the mark on the roller, so that each pattern was produced by the same portion of the engraving.

The method used for the extraction was that of Abramovitch⁸ employing an aqueous Cellosolve-caustic soda-sodium hydrosulphite liquor. The extraction liquor was formulated as follows—

30 c.c.	...	Cellosolve (β -ethoxyethanol)
2 c.c.	...	Caustic soda (68°Tw.)
1 g.	...	Sodium hydrosulphite
0.2 c.c.	...	Dispersol VL

Made up to 100 c.c. with Distilled water

The actual size of the patterns varied with the dye according to the optical density of the resultant solution, but for a medium depth of colour it was generally about 1 in. square. The pattern was placed in a flask, and 30 c.c. of extraction liquor added. The flask was heated for 10 min. on a boiling water bath with occasional shaking, and the liquor then decanted into a 100-ml. standard flask. The extraction was repeated twice, and after being cooled the standard flask was made up to volume. The optical density of the resultant leuco dye solution was then measured on the Spekker (Hilger) absorptiometer. In the case of the unfixed prints a correction was found necessary to compensate for the effect of the thickener which was also present in the prints. A further allowance had to be made for the shrinkage of the fixed prints which occurred during the finishing processes. Each measurement was made in duplicate, and in practically all cases excellent agreement obtained. When obvious discrepancies were apparent, the measurements were checked by repeat experiments.

This extraction procedure proved satisfactory for all the Caledon-type dyes but failed with the Durindone dyes owing to the instability of the leuco dye solutions. For the latter dyes a method based on that of Lotichius⁹ was employed. The patterns were dissolved in cold concentrated sulphuric acid, and the dye was precipitated by running the solution into cold water containing a dispersing agent, Dispersol VL. The resultant fine suspensions could be measured accurately on the absorptiometer. In addition to corrections for thickening and shrinkage, allowance in this instance has also to be made for the absorption due to the charring of the cloth by the strong acid.

Results

EXPRESSION OF RESULTS

The basic measurement used throughout this work was the percentage fixation of the vat dye obtained by measuring the amount of dye fixed on the fabric after all or part of the finishing processes had been completed. By extracting the dye from standard patterns cut from (i) unsteamed prints and (ii) finished prints, the results could be expressed as follows—

$$\text{Dye fixation (\%)} = \frac{\text{Dye fixed on fibre}}{\text{Dye originally applied}} \times 100$$

The results were shown in graphical form—in the case of the Formosul variations, for example, by plotting percentage dye fixation against the Formosul content of the print paste. In other cases it was found more convenient to plot dye fixed against dye applied.

FORMOSUL SENSITIVITY

The graphs reproduced in Fig. 1-5 show the sensitivity to Formosul concentration of five of the seventeen vat dyes examined by the potassium carbonate-Formosul process. Each dye was printed in a British gum thickening containing 13.5% potassium carbonate and 5% glycerol together with a Formosul content varying from 0 to 16%. The graphs show that for most vat dyes a fixation of 75-95% can be achieved. The shapes of certain

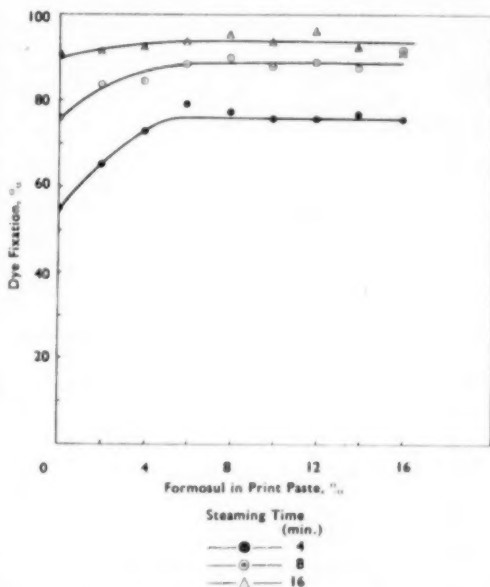


FIG. 1—Formosul Sensitivity of 10% Caledon Printing Yellow GNS Paste

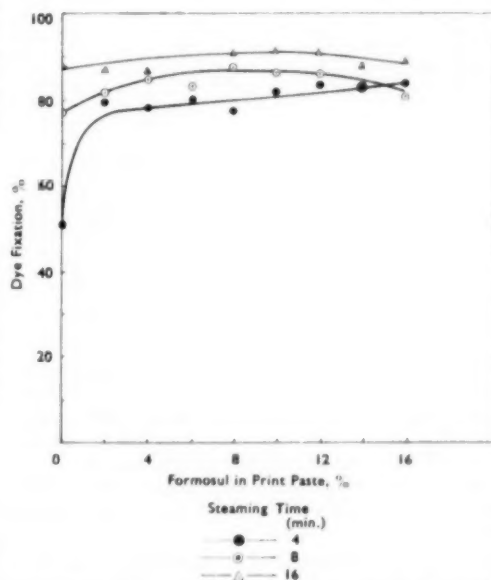


FIG. 2—Formosul Sensitivity of 5% Durindone Printing Blue 4 BCS Paste

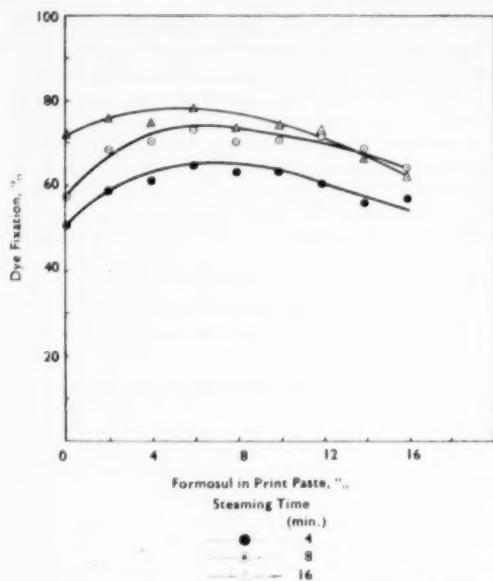


FIG. 3—Formosul Sensitivity of 10% Caledon Printing Red BNS Paste

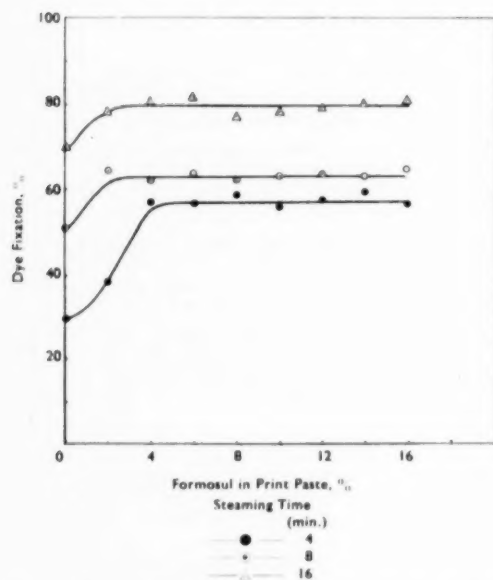


FIG. 4—Formosul Sensitivity of 10% Durindone Printing Red 3BS Paste

graphs show how critical are the conditions with certain dyes, e.g. cf. Caledon Printing Yellow GNS Paste (Fig. 1) with Caledon Brown RS Paste Fine (Fig. 16). The latter is also shown to be susceptible to over-reduction and destruction.

The results obtained show that vat dyes may be divided into the following three broad categories—

(a) Dyes which are largely insensitive to alterations in the Formosul concentration in the printing paste, e.g. Caledon Printing Yellow GNS Paste (Fig.

1) and Durindone Printing Blue 4BCS Paste (Fig. 2). These and similar dyes can be relied upon to give reproducible results under a wide range of conditions by either roller or screen printing, and show little loss in fixation even when no Formosul

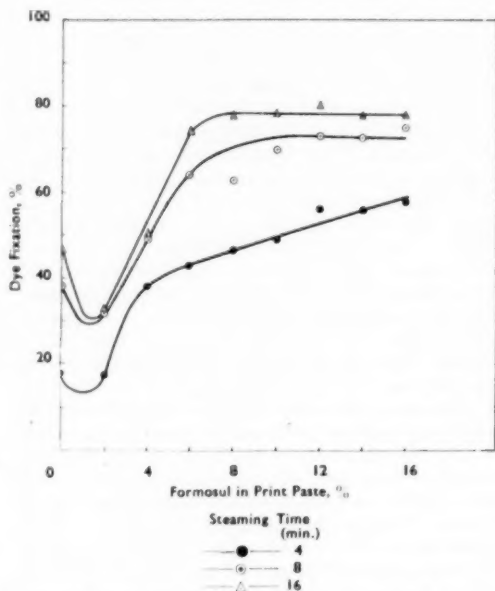


FIG. 5—Formosul Sensitivity of 10% Durindone Printing Brown GS Paste

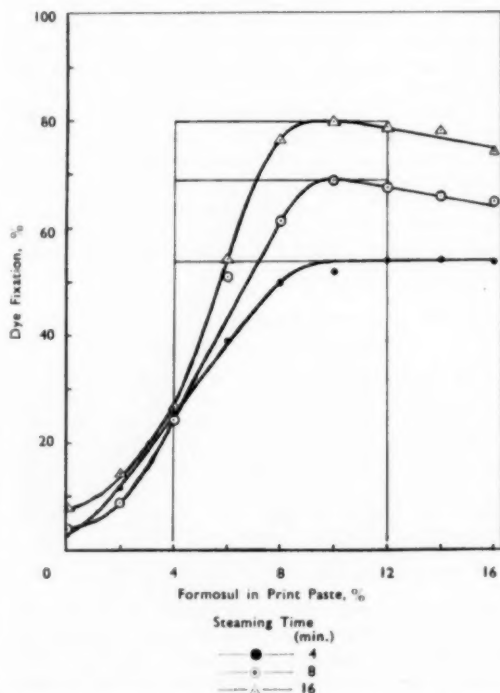


FIG. 6—Formosul Sensitivity of 10% Caledon Printing Yellow 5GS Paste

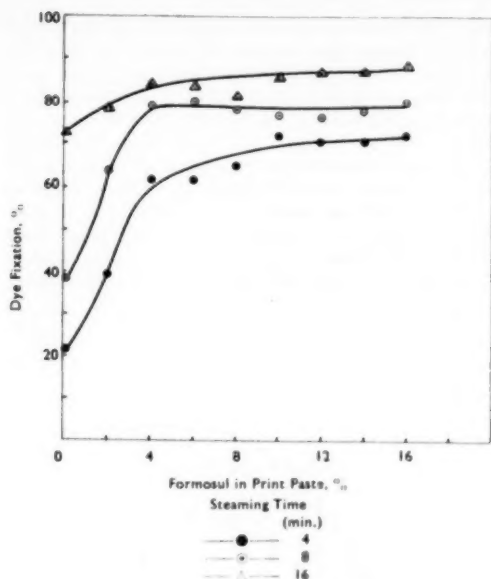


FIG. 7—Formosul Sensitivity of 10% Caledon Printing Orange 6RS Paste

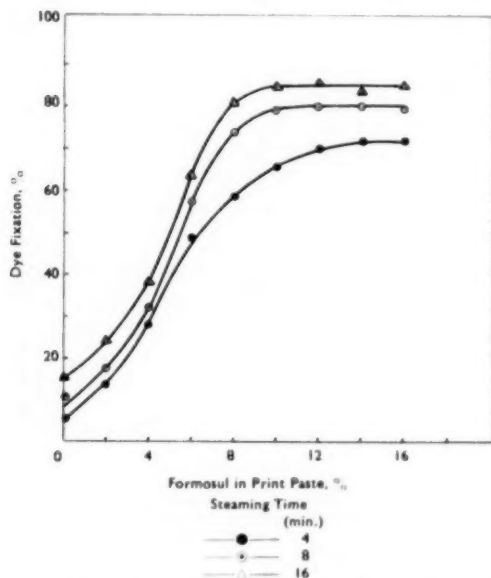


FIG. 8—Formosul Sensitivity of 10% Caledon Printing Brown 4RS Paste

is added to the printing paste provided that British gum thickening is used. This thickening has fairly powerful reducing properties itself, being able to reduce vat dyes in this category.

(b) Dyes which require a specific "threshold" concentration of Formosul to be present in order that satisfactory fixation may be obtained. If the Formosul falls below this concentration, the percentage fixation of the dye falls away very sharply. Examples of this class of dye—Durindone Printing Brown GS and Caledon Printing Yellow

5GS Paste—are shown in Fig. 5 and 6. The threshold concentrations for dyes in this class vary over a considerable range, and where the value is low the dye will generally give satisfactory results under practical conditions. When the threshold concentration is high, however, even though allowance is made by increasing the original concentration of reducing agent in the printing paste, it is inadvisable to delay ageing of the prints, otherwise inferior fixation will be obtained owing to decomposition of the Formosul on the print by air

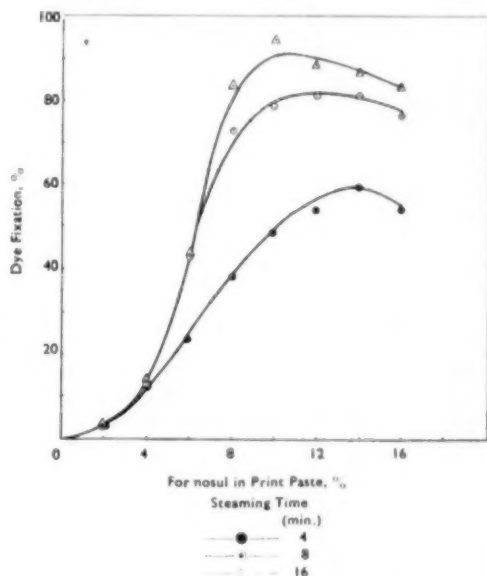


FIG. 9—Formosul Sensitivity of 7.5% Caledon Printing Red 3B 200 Paste

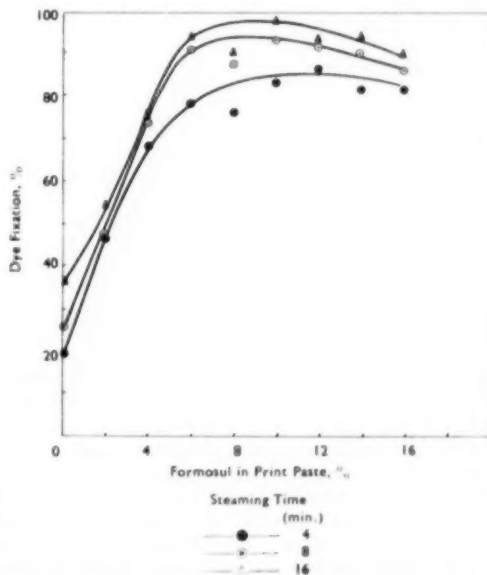


FIG. 10—Formosul Sensitivity of 5% Caledon Printing Purple 4RS Paste

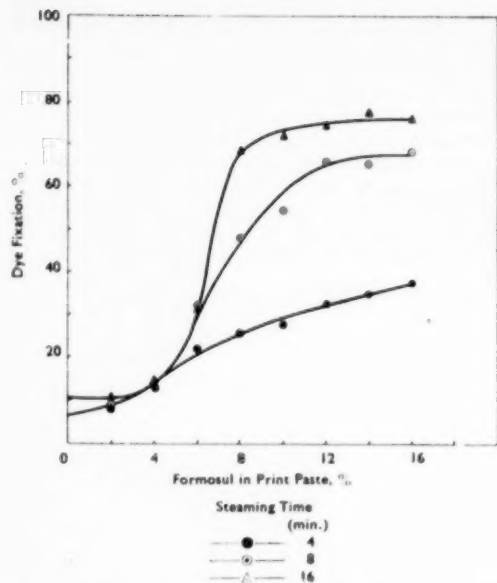


FIG. 11—Formosul Sensitivity of 10% Caledon Brilliant Violet RS Paste Fine

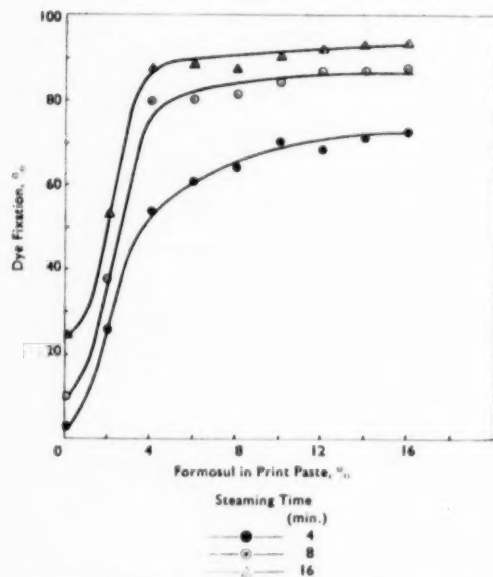


FIG. 12—Formosul Sensitivity of 5% Caledon Printing Jade Green XBNS Paste

oxidation. Dyes of this latter type are particularly difficult to apply under screen printing conditions.

(c) Dyes which are hypersensitive to the Formosul concentration in the print paste. The outstanding example here is Caledon Brown RS Paste Fine (Fig. 16), a dye which requires a high concentration of the reducing agent for satisfactory fixation, coupled with a long steaming period, and which is susceptible to over-reduction at still higher concentrations. This graph is exceptionally interesting, since it demonstrates very clearly the reason

why this dye is not normally employed by the textile printer. In the first place it is quite clear that the dye may be reduced satisfactorily under printing conditions, and in fact it would be quite satisfactory if the conditions could be stabilised within narrow limits. Owing to the fact that Formosul is not stable, particularly when exposed to the atmosphere as on a print, control within these fine limits is extremely difficult under bulk working conditions.

Previously no numerical function has been available for classifying vat dyes according to their printing properties, but the graphs now presented

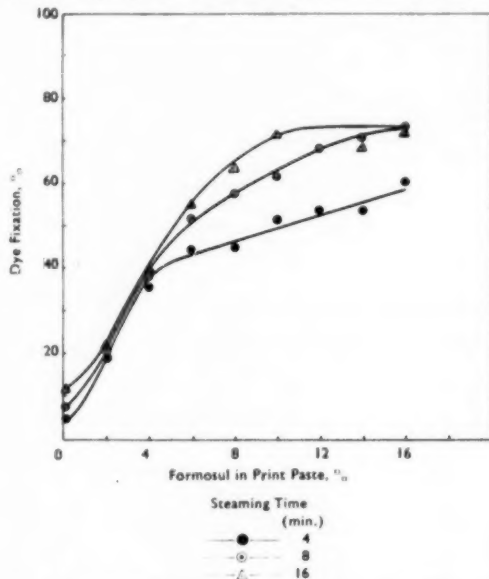


FIG. 13—Formosul Sensitivity of 15% Caledon Printing Green RCS Paste

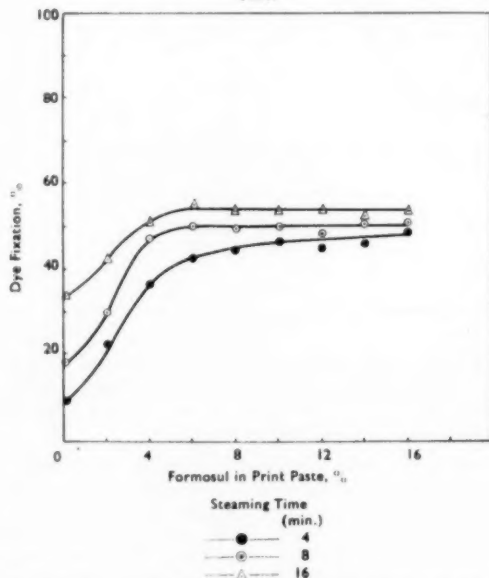


FIG. 14—Formosul Sensitivity of 10% Durindone Printing Scarlet Y8 Paste

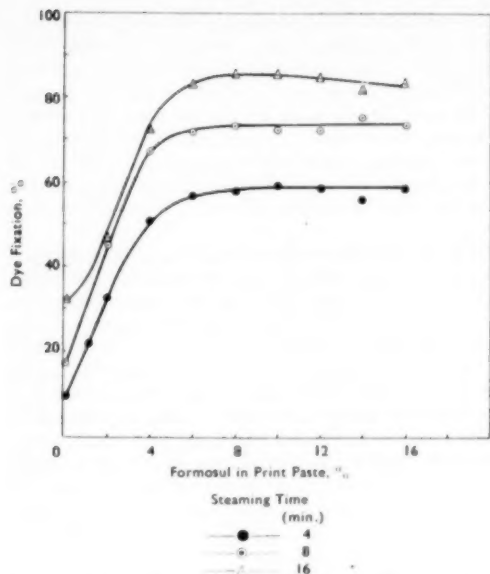


FIG. 15—Formosul Sensitivity of 10% Durindone Printing Pink FFS Paste

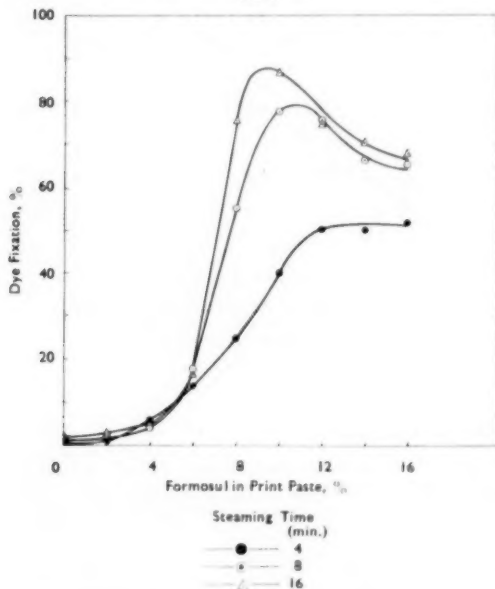


FIG. 16—Formosul Sensitivity of 15% Caledon Brown RS Paste Fine

can be interpreted to give such a grading. Vertical lines were drawn on the graphs corresponding to Formosul concentrations of 4% and 12%, it being considered that this range covers the concentrations likely to be experienced under practical conditions. Horizontal lines were added through the maximum percentage dye fixation values within the prescribed Formosul concentrations for each of the three steaming times (see Fig. 6). The area under each curve was then expressed as a percentage of the area of the corresponding rectangle, and the three results, obtained for each dye with the three

steaming times of 4, 8, and 16 min., were averaged. The "Formosul sensitivity index" was obtained by expressing the results on a 1-9 scale as in Table I.

TABLE I

Formosul Sensitivity Index	Area under curve Area of rectangle $\times 100$
9	100-95
8	95-90
7	90-85
6	85-80
5	80-75
4	75-70
3	70-65
2	65-60
1	< 60

It is considered that this method of assessment gives a fair representation of the behaviour which may be expected from the dye under practical conditions. The values obtained for the seventeen dyes studied are given in Table II, together with the Formosul concentrations necessary to obtain 90% of maximum fixation with steaming times of 4 and 16 min. The maximum percentage dye fixation value corresponds to a steaming time of 16 min.

RATE OF FIXATION

From the relative positions of the three curves corresponding to steaming times of 4, 8, and 16 min. an indication of the time necessary to obtain maximum fixation may be deduced. This is much more clearly revealed, however, by studying the curves relating steaming time and percentage fixation of the dyes. These curves were obtained by printing each dye with its optimum Formosul concentration, the steaming time being varied from 1 to 40 min. They are asymptotic in form, so that selection of the point of maximum fixation is difficult. Therefore the time needed to give 90% of

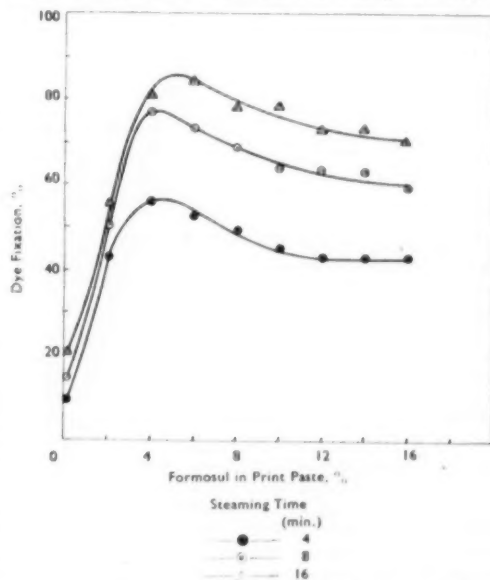


FIG. 17—Formosul Sensitivity of 15% Caledon Printing Blue GCPs Paste

maximum fixation has been used to obtain a grading for the dyes (see Table II). The least satisfactory dyes, such as Caledon Printing Yellow 5GS Paste (Fig. 18), show a continual increase in percentage fixation with time, so that even after 40 min. equilibrium has not been attained. For most dyes equilibrium is reached much more rapidly, 90% of the maximum fixation being reached, for example, in 3.0 min. with Durindone Printing Blue 4BCS Paste and in 11.6 min. with Durindone Printing Pink FF 125 Paste (Fig. 18).

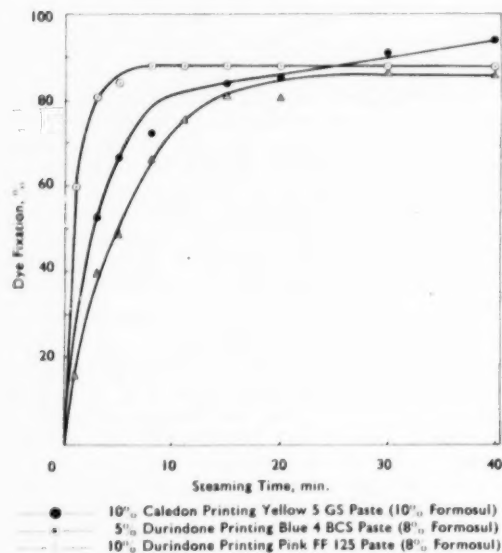


FIG. 18—Rate of Fixation

BUILDING-UP PROPERTIES

The building-up properties of the dyes were studied by printing them at varying concentrations in the presence of optimum Formosul print paste

concentrations and steaming for the optimum period. The resultant graphs enable selection to be made of those dyes which yield a straight-line relationship between dye fixed and dye applied right up to heavy depths as in the case of Caledon Printing Jade Green XBNS Paste (Fig. 19). At the other extreme Caledon Printing Red BNS Paste (Fig. 19) shows a marked falling away from the straight-line relationship when printed stronger than 8%.

The results obtained for the range of dyes studied are given in the last column in Table II. Building-up has been defined in terms of the proportion of dye fixed when 20% dye is applied, expressed as a percentage of the fixation which would be obtained if the initial straight-line portion of the building-up curve had been maintained. In certain cases, e.g. Caledon Printing Red BNS paste, a very deep colour was obtained at less than 20% application, and the building-up was measured at a lower concentration (as indicated in brackets in Table II).

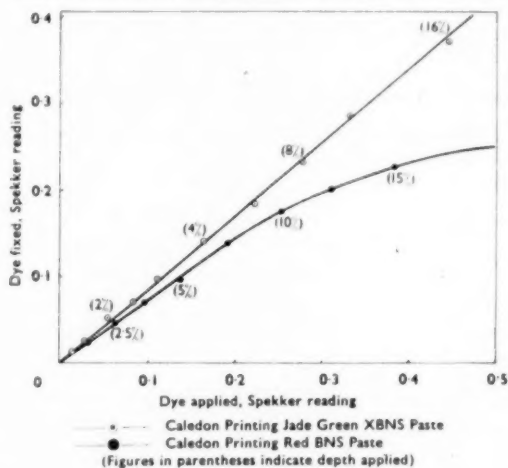


FIG. 19—Building-up Properties

TABLE II
Sensitivity to Formosul of Vat Dyes

Dye	Formosul Concn. for 90% of Max. Fixation (%)		Max. Fixation (16 min. steaming) (%)	Area under curve $\times 100$		Formosul Sensitivity Index	Steaming Time for 90% of Max. Fixation (min.)	Building-up Properties (% of rectilinear value at 20% application)
	Steamed 4 min.	Steamed 16 min.		Area of rectangle				
Caledon Printing Yellow 5GS Paste	7.7	7.4	80.0	83.6		6	15.1	85
Caledon Printing Yellow GNS Paste	2.7	0.0	93.4	99.3		9	4.5	92.5
Caledon Printing Orange 6RS Paste	5.8	1.5	86.5	97.9		9	5.5	100
Caledon Printing Brown 4RS Paste	9.4	7.2	83.0	83.3		6	6.4	92
Caledon Brown RS Paste Fine	10.8	8.1	87.8	58.8		1	6.7	96.5
Durindone Printing Brown GS Paste	12.2	5.6	78.2	89.6		7	7.5	77.5
Durindone Printing Scarlet YS Paste	6.1	3.3	54.5	98.1		9	11.0	100
Durindone Printing Pink FF 125 Paste	4.6	4.5	85.0	98.0		9	11.6	90.5
Caledon Printing Red BNS Paste	2.3	0.0	78.4	97.8		9	3.7	66 (15%)
Durindone Printing Red 3BS Paste	3.4	0.5	79.6	99.9		9	11.0	92
Caledon Printing Red 3B 2C0 Paste	10.9	8.0	92.1	71.3		4	7.5	89.5
Caledon Printing Purple 4RS Paste	5.5	5.1	97.6	96.6		9	7.2	100 (15%)
Caledon Brilliant Violet RS Paste Fine	13.2	8.0	75.9	73.6		4	8.7	100
Durindone Printing Blue 4BCS Paste	1.6	0.0	90.8	99.3		9	3.0	85.5 (15%)
Caledon Printing Blue GCPS Paste	2.7	3.4	86.0	89.8		7	8.1	78
Caledon Printing Jade Green XBNS Paste	7.7	3.5	93.5	94.7		8	3.9	100 (16%)
Caledon Printing Green RCS Paste	12.0	8.1	73.0	85.8		7	7.1	100

ALKALI CONTENT OF PRINTING PASTES

The effect of variation of the other components of vat-dye printing pastes has also been studied. Caledon Printing Jade Green XBNS Paste and Caledon Brown RS Paste Fine were selected to represent dyes having good and poor printing properties respectively. These dyes were printed with varying amounts of three alkalis—potassium carbonate, sodium carbonate and caustic soda—and steamed for 4, 8, and 16 min.

With potassium carbonate, shortening of the steaming time resulted in considerable lowering in the percentage fixation obtained (Fig. 20). The optimum concentration of potassium carbonate was shown to be 9–10%, a value lower than that generally employed in the textile-printing trade.

When sodium carbonate is used in the preparation of printing pastes, a top limit of 6% is set on the permissible concentration owing to its low solubility. From the graphs obtained (Fig. 21) it was

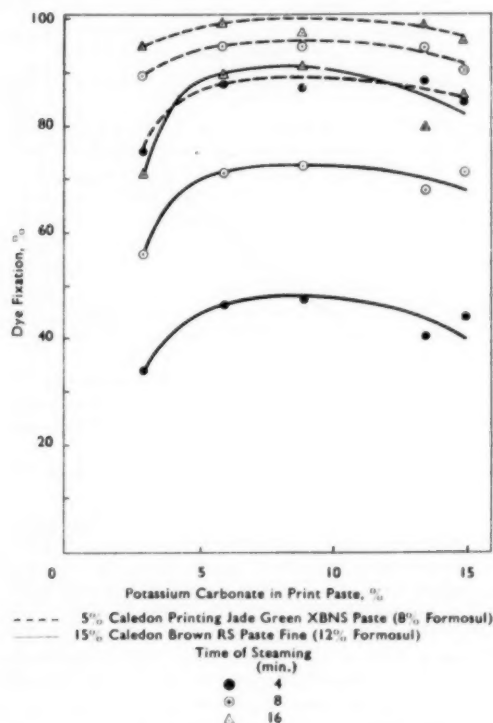


FIG. 20—Alkali Variations—Potassium Carbonate

apparent that this concentration was barely sufficient to permit maximum fixation to be realised, particularly with short steaming times, and the equilibrium values were a little inferior to those obtained with potassium carbonate. Under optimum Formosul concentration conditions, equilibrium fixation was attained more rapidly with sodium carbonate than with potassium carbonate. Some inconsistency in the results was noted in the case of sodium carbonate, but it was considered that this was due to an attempt being made to

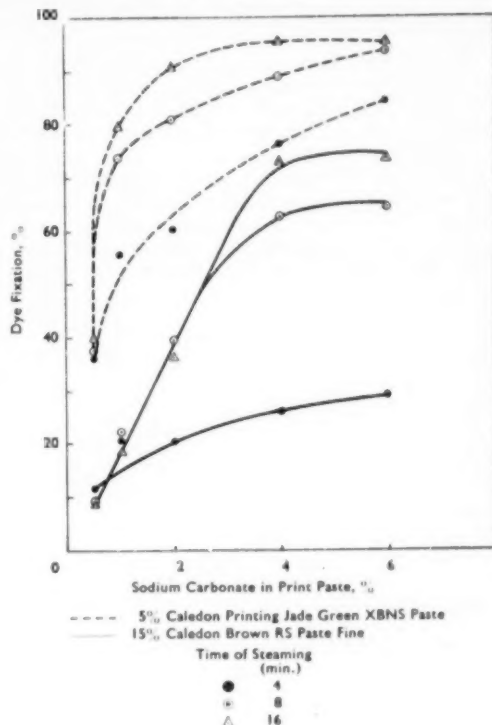


FIG. 21—Alkali Variations—Sodium Carbonate

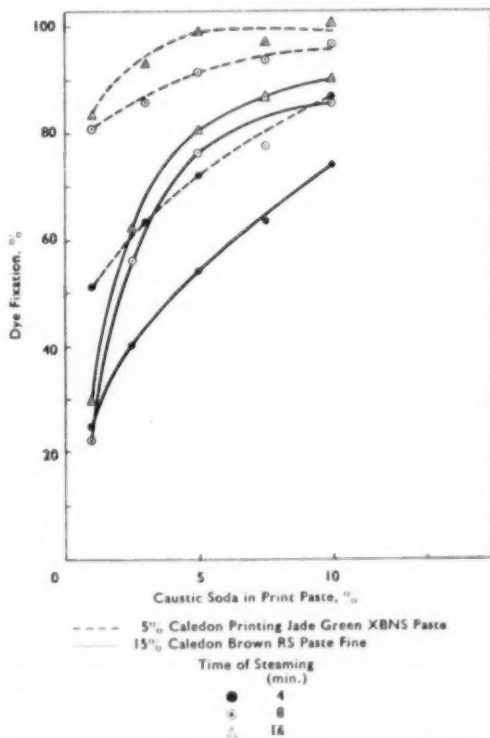


FIG. 22—Alkali Variations—Caustic Soda

prepare print pastes at maximum solubility of this alkali.

When caustic soda was used as the alkali in vat-dye printing pastes, there was a general increase in the yield obtainable with each of the three steaming times, and the prints were much less susceptible to variations in steaming time. The optimum caustic soda concentration was greater than 10% of the weight of printing paste (Fig. 22). In this case it may well be that the swelling action of caustic soda on the fibre plays a part, but generally caustic soda preparations tend to be unstable to storage,

part when superheated steam is present in the steamer. In addition, glycerol may possibly exert a solubilising influence on the leuco vat dye.

FORMOSUL : DYE RATIO

The variations in the Formosul content of the print paste necessary for different dye concentrations have been studied for one dye—Caledon Printing Red 3B 200 Paste. The outstanding feature was that, even at very low depths (1.25%), a minimum concentration of approx. 6% Formosul was necessary in order to obtain fixation of this dye (Fig. 24). For depths of 20% (i.e. 16 times as strong as the weak prints), it was necessary to increase the reducing agent only to approx. 10% in order to obtain satisfactory fixation. From the practical viewpoint it appeared, therefore, that "reduction thickeners"* should contain an equal concentration of Formosul to that present in the initial stock paste in order to ensure that no serious loss in fixation occurred when intermediate depths were printed.

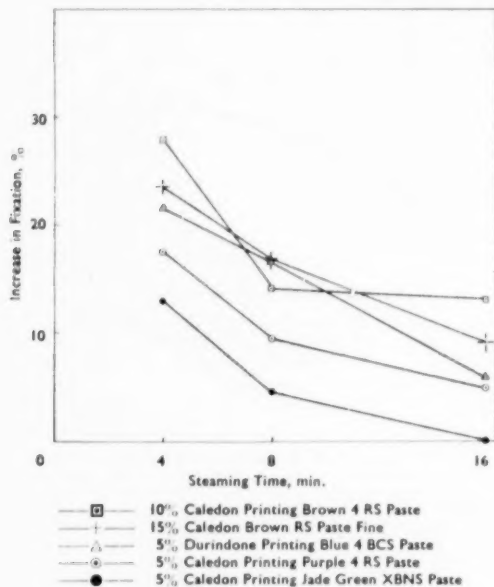


Fig. 23—Effect of adding 5% Glycerol to the Print Paste

and so the advantage is lost. Some experimental inconsistencies were also noted with caustic soda print paste preparations, possibly due to the formation of sodium carbonate.

GLYCEROL CONTENT OF PRINTING PASTES

The effect of the addition of glycerol to the print paste has been examined for a range of five dyes. Prints were prepared from print pastes containing standard quantities of the other ingredients, but one contained no glycerol and the other 5% glycerol. The effect of the glycerol was most marked with short steaming times, the average percentage increase in fixation after 4 min. steaming being a little over 20% for the dyes employed. As the time of steaming was increased the advantage gained from adding glycerol decreased, until after 16 min. steaming the average percentage increase in fixation was less than 7% (Fig. 23).

These results have been obtained under laboratory steaming conditions, where the bulk of the cloth relative to the capacity of the steamer is small compared with commercial agers, and it is obvious that a fuller investigation into the effect of glycerol and similar hygroscopic agents is desirable. It is well recognised that such substances play a major

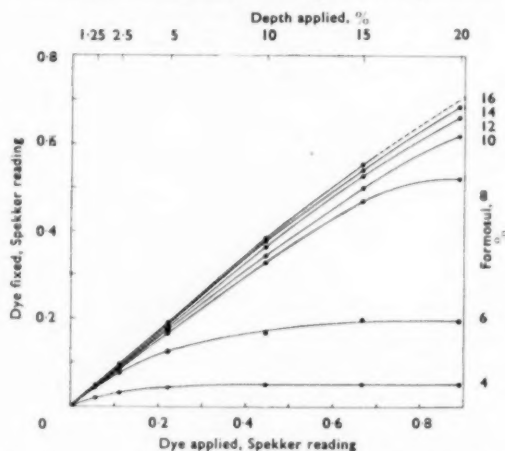


Fig. 24—Formosul : Dye Ratio for Caledon Printing Red 3B 200 Paste

An observation of this kind clearly emphasises the problems facing a practical vat-dye printer. For obvious reasons he wishes to use as far as practicable standard stock thickenings and formulations. Here is an example of a dye requiring high concentrations (6%) of Formosul in pale shades, whereas Caledon Printing Blue GCPS Paste (Fig. 17) is markedly affected by over-reduction under similar conditions with Formosul concentrations above 5% for a depth of 15%.

A case of a dye which is intermediate between these two extremes is Caledon Printing Jade Green XBNS Paste, which requires an increase in Formosul concentration from 4% to 8% when the depth of shade is increased from 5% to 20% (Fig. 25).

EFFECTS OF THICKENING AGENTS

Caledon Printing Jade Green XBNS Paste and Caledon Brown RS Paste Fine, representing dyes possessing good and poor printing properties respectively, have been applied under identical conditions in four different thickenings with a

* Thickenings containing no dye, used to dilute printing pastes.

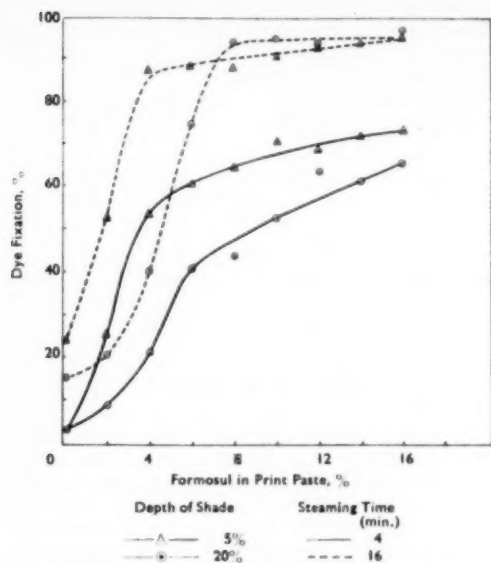


FIG. 25—Formosul Sensitivity of Caledon Printing Jade Green XBNS Paste in 5% and 20% Depths

constant Formosul-alkali formulation. No attempt was made to obtain pastes of equal viscosity, and in this respect the pastes varied widely.

Despite this difference, it was found that very nearly equal amounts of dye and hence of printing paste were applied to the fabric in every case. In addition, although the prints showed marked differences in strength when assessed visually, the percentage fixation of the dyes was practically identical (Fig. 26 and 27).

In view of the high percentage fixation obtained for the dyes, the results indicate that the leuco vat dye has little affinity for the thickening relative to its affinity for cellulose. This point is further

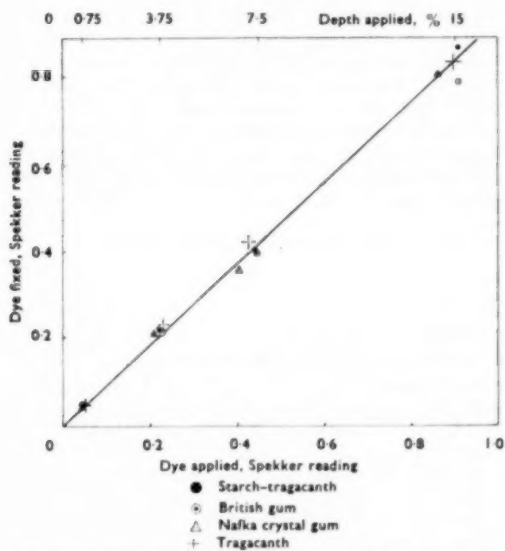


FIG. 26—Caledon Printing Jade Green XBNS Paste in Various Thickenings

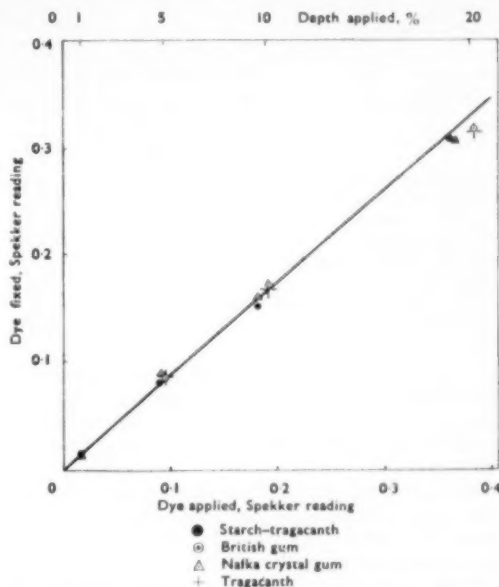


FIG. 27—Caledon Brown RS Paste Fine in Various Thickenings

emphasised by the very slight differences in percentage fixation which were obtained when different thickening agents were employed.

The study of printing thickenings is a very complicated field, requiring extensive study to enable a complete understanding to be arrived at. It is not proposed, therefore, to attempt in this paper to establish more than the almost equal printing efficiency of the several gums examined.

One observation, however, is worth recording regarding starch thickenings, which are commonly employed in order to obtain prints having increased visual strength compared with those obtained with British gum thickenings. In one series of experiments a relatively thin starch thickening was used, and this gave well penetrated, smooth, visually weak prints compared with a rather thick British gum thickening. This effect is probably due to the fact that the thixotropy of starch thickenings decreases with dilution, so that in this experiment there was less setting up of the starch paste when the high stresses present during the printing process were removed, resulting in the more completely penetrated print.

PROCESS VARIATION AFTER STEAMING

The method used for estimating the percentage of dye fixed under given conditions is very suitable for studying the losses which occur at various stages of processing. The processing of patterns can be halted at any stage, and the amount of dye lost in any one of the finishing processes measured.

The main use which has so far been made of this technique has been to determine the losses which occur during the washing off, oxidising, and soaping of prints, and to decide whether the order of processing is important. For most of the Caledon dyes examined, washing-off in water prior to oxidation resulted in rather greater losses of dye than if

TABLE III
Processing Losses

(Dye fixation (%) after stated treatment. Formosul ... 8%)								
Processing given to Patterns			10% Caledon Printing Yellow GNS Paste (Steamed 15 min.)		5% Caledon Printing Jade Green XBNS Paste (Steamed 8 min.)		10% Durindone Printing Brown GS Paste (Steamed 12 min.)	
			Unsoaped	Soaped	Unsoaped	Soaped	Unsoaped	Soaped
Printed, unsteamed	100	—	100	—	100	—
Printed, steamed	94.6	—	100	—	86.3	—
Printed, steamed, oxidised in running water	93.0	84.8	94.5	91.4	74.6	72.0
Printed, steamed, oxidised with neutral dichromate	95.7	92.2	93.0	94.0	78.0	76.4
Printed, steamed, oxidised with acid dichromate	96.7	93.5	92.5	88.3	77.9	75.3

an oxidation bath was used (see Table III). Subsequent soaping of these prints produced very nearly equal losses of dye, so that the chemically oxidised prints remained rather stronger than the water-oxidised prints.

Examination of the Durindone types revealed that part of the dye was destroyed during the steaming process, but the exact mechanism of this decomposition is not known.

With both Durindone Printing Brown GS Paste and Durindone Printing Scarlet YS Paste (Tables III and IV) improved yields were obtained by dichromate oxidation, but with the latter dye this resulted in severe dulling of the print. With Durindone Printing Scarlet YS Paste superior fixation was obtained from water oxidation compared with peroxide oxidation if processing must follow ageing, but after the prints had been hung in air the two methods of oxidation gave very similar results. The problems associated with the washing-off of vat dyes of the Durindone Scarlet YS Paste type are well known, and so far research has revealed no complete solution to the problem.

DYE LOSSES DURING THE PRINTING PROCESS

During the machine printing of multicolour patterns the colour applied by the first printing roller is subjected to "crushing" by the subsequent printing rollers, and part of the print paste originally applied will be removed by these rollers. To avoid excessive adulteration of the later printing pastes, lint doctors are frequently used in practice, and serve to pick up from the roller surfaces not only lints but also the colour paste which has been removed from the designs applied to the cloth by earlier printing rollers. It was considered desirable

to attempt to measure the amount of dye lost in this manner.

The experimental work was carried out on a three-colour machine. Initially all three rollers were in use producing a striped pattern; at a later stage the third printing roller was "dropped back", and later again the second. In this way it was possible to obtain a printed stripe which had been subjected to no crush, to one crush, or to two crushes. Two trials were carried out, firstly with a vat-dye printing paste based on British gum and secondly with one based on starch-tragacanth. The engraving of the first printing roller had been partly blocked to identify a portion of the circumference of the roller, so that patterns for extraction could be cut out which had been applied by the same portion of the engraving. By estimating the dye present in standard-sized patterns cut from the prints it was possible to estimate the amount of dye removed from the prints by the subsequent crushes.

The losses obtained with a starch-tragacanth thickening are greater both under the first and second crushes than when British-gum thickenings are used (Table V). With both thickenings the greatest loss is experienced at the first crush. Visually it appeared that much greater losses were sustained with the starch-tragacanth thickening than was accounted for by the actual measured loss in dye. However, when attempts were made to assess the loss in visual strength and a range of strengths was printed with the two thickenings, it became apparent that much superior build-up was obtained with starch-tragacanth. As a result, the rather greater losses sustained on crushing with

*Roller removed from contact with fabric

TABLE IV
Processing Losses

(10% Durindone Printing Scarlet YS Paste printed with 8% Formosul and steamed for 8 min.)
(Dye fixation (%) after stated treatment)

Processing given to Patterns	Processed immediately		Processed after 3 days' Hanging	
	Unsoaped	Soaped	Unsoaped	Soaped
Printed, unsteamed	100	—	—	—
Printed, steamed	81.2	—	—	—
Printed, steamed, oxidised in running water	48.4	36.2	69.7	55.0
Printed, steamed, oxidised with neutral dichromate	72.8	60.6	80.7	64.5
Printed, steamed, oxidised with acid dichromate	73.8	62.7	77.9	60.4
Printed, steamed, oxidised with H ₂ O ₂	37.7	28.8	68.3	55.2

TABLE V
Dye Losses due to "Crushing" on Printing Machine
(5% Caledon Printing Jade Green XBNS Paste)

	Spekker Reading		Dye Fixation (%)		Loss (%)	
	British Gum	Starch-Tragacanth	British Gum	Starch-Tragacanth	British Gum	Starch-Tragacanth
Dye applied by first printing roller ...	0.392	0.394	100	100	—	—
Dye remaining after one crush ...	0.363	0.356	92.7	90.5	7.3	9.5
Dye remaining after two crushes ...	0.346	0.333	88.4	84.5	11.6	15.5

this thickener were exaggerated by visual assessment, whereas British gum with its relatively poor build-up was not affected to the same degree.

COMPARISON OF PRINTING PROPERTIES ON COTTON AND ON VISCOSE RAYON

A comparison of the printing properties of vat dyes on cotton and on viscose rayon staple has been made by selecting four dyes from those in Table II, printing them on viscose rayon staple, and drawing graphs showing their Formosul sensitivities and rates of fixation (Fig. 28-35).

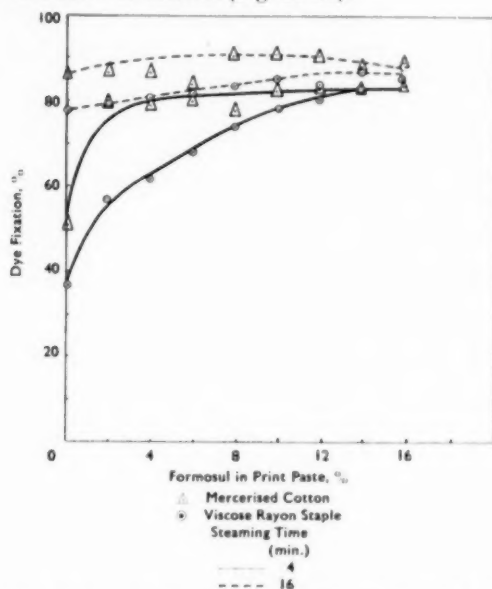


FIG. 28—Formosul Sensitivity of 5% Durindone Printing Blue 4BCS Paste on Mercerised Cotton and Viscose Rayon Staple

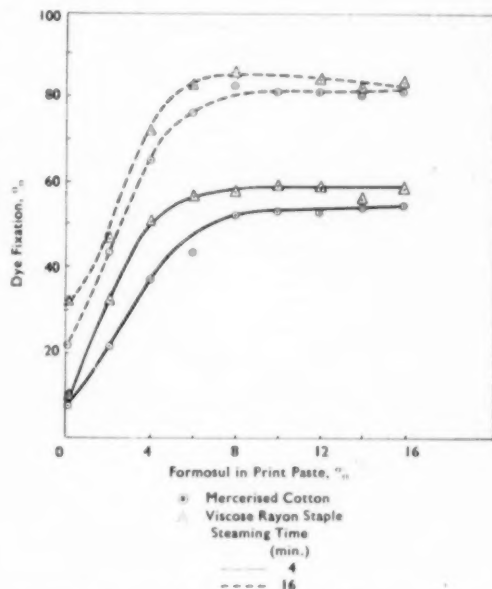


FIG. 29—Formosul Sensitivity of 10% Durindone Printing Pink FFS Paste on Mercerised Cotton and Viscose Rayon Staple

The dyes selected were two of the Durindone type—Durindone Printing Blue 4BCS Paste (Fig. 28 and 32) and Durindone Printing Pink FFS Paste (Fig. 29 and 33)—and two of the Caledon type—Caledon Printing Jade Green XBNS Paste (Fig. 30 and 34) and Caledon Printing Red 3B 200 Paste (Fig. 31 and 35); each pair comprised a dye which showed good printing properties on cotton and one which showed poor printing properties.

The graphs showed that, for the vat dyes examined, there is a close resemblance between the

TABLE VI
Comparison of Viscose Rayon Staple with Mercerised Cotton

Dye	Material*	Formosul Concn. for 90% of Max. Fixation (%)		Maximum Fixation (16 min. steaming)	Area under Curve / Area of Rectangle × 100	Formosul Sensitivity Index	Steaming Time for 90% of Max. Fixation (min.)
		Steamed 4 min.	Steamed 16 min.				
Caledon Printing Jade Green XBNS Paste	V	3.8	2.5	96	99.3	9	3.4
	M	7.7	2.5	93.5	94.7	8	3.9
Caledon Printing Red 3B 200 Paste	V	10.6	10.2	95	67.3	3	11.6
	M	10.9	8.0	92.1	71.3	4	7.5
Durindone Printing Pink FF 125 Paste	V	6.4	5.2	81.5	93.7	8	9.4
	M	4.6	4.5	85.0	98.0	9	11.6
Durindone Printing Blue 4BCS Paste	V	8.3	1.2	87.5	89	7	4.0
	M	1.6	0.0	90.8	99.3	7	3.0

* M. Mercerised cotton
V. Viscose rayon staple

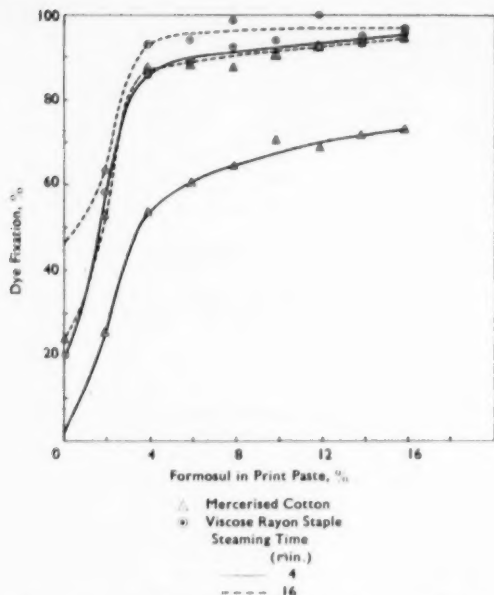


FIG. 30—Formosul Sensitivity of 5% Caledon Printing Jade Green XBN8 Paste on Mercerised Cotton and Viscose Rayon Staple

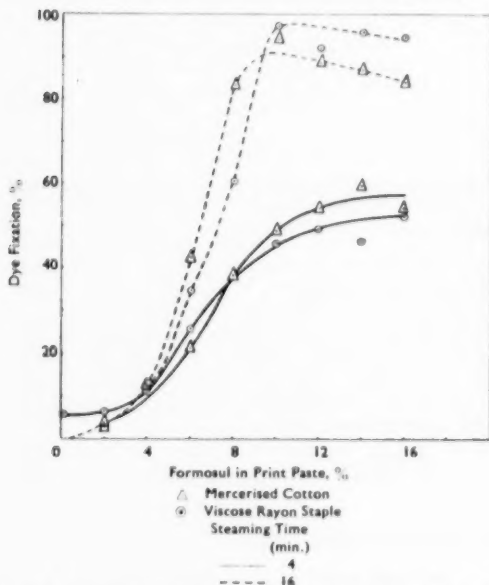


FIG. 31—Formosul Sensitivity of 7.5% Caledon Printing Red 3B 200 Paste on Mercerised Cotton and Viscose Rayon Staple

printing properties on cotton and on viscose rayon. A summary of the printing properties is given in Table VI.

These results do not confirm the difficulties experienced in the trade with the printing of spun viscose. However, this work was carried out under rigidly controlled laboratory steaming conditions, and preliminary investigations into the effects of variations in steaming conditions have confirmed that such variations are largely responsible for the printing difficulties with vat dyes on spun viscose.

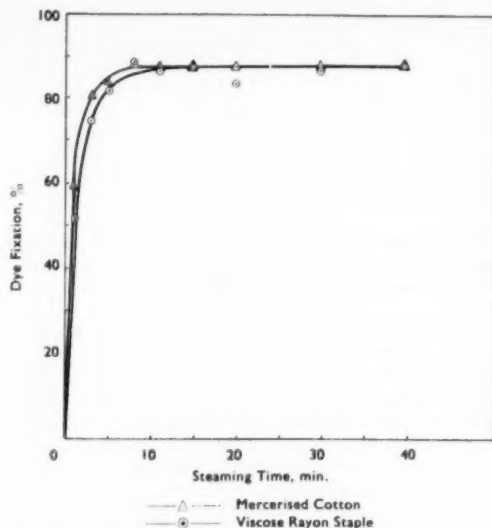


FIG. 32—Rate of Fixation of 5% Durindone Printing Blue 4BCS Paste on Mercerised Cotton and Viscose Rayon Staple

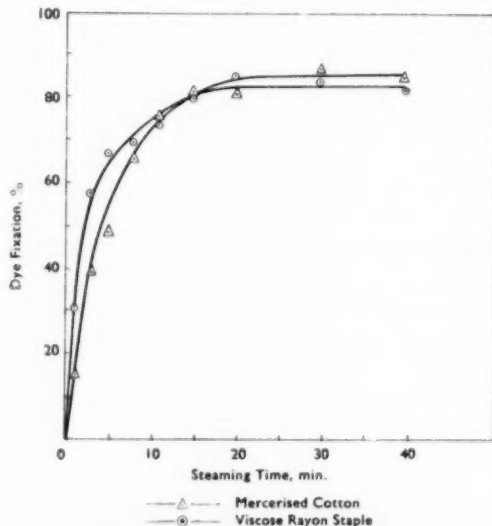


FIG. 33—Rate of Fixation of 10% Durindone Printing Pink FFS Paste on Mercerised Cotton and Viscose Rayon Staple

Preliminary Observations on the Pad-Steam Process

The pad-steam process, which we have investigated, involved printing the dispersed vat dye in a thickening which is insolubilised by alkalis. Prior to steaming the prints are padded through a potassium carbonate-Formosul liquor, and are usually passed straight into the steamer without intermediate drying and steamed for periods up to 20 min. This steaming time is considerably greater than the 15-60 sec. now being claimed for the "flash steam" process in the U.S.A.¹⁰ and in view of the statements made earlier regarding the rate of fixation of vat dyes under printing conditions when

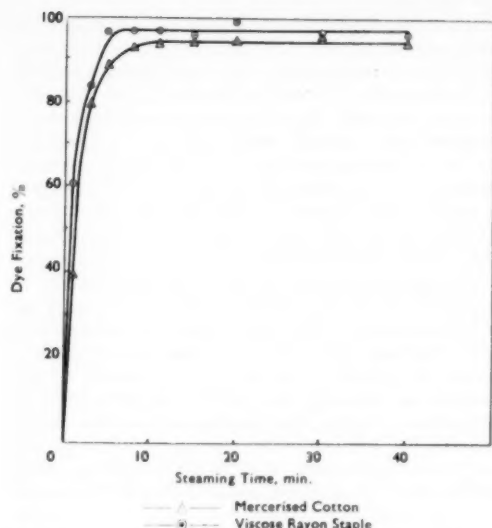


Fig. 34—Rate of Fixation of 5% Caledon Printing Jade Green XBN8 Paste on Mercerised Cotton and Viscose Rayon Staple

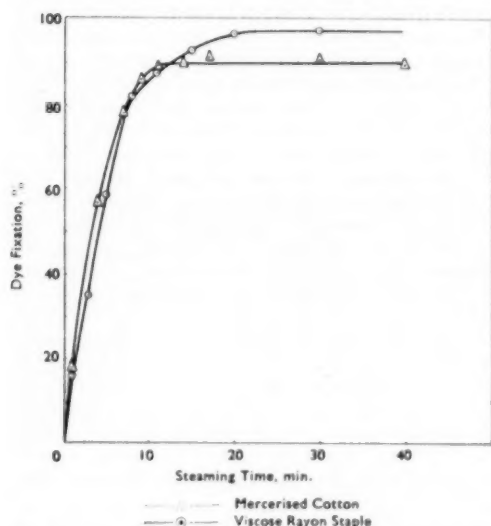


Fig. 35—Rate of Fixation of 7.5% Caledon Printing Red 3B 200 Paste on Mercerised Cotton and Viscose Rayon Staple

the potassium carbonate-Formosul process is used, the technically curious must be wondering how to reconcile the yields described with steaming times of 10–20 min. and those now being claimed with steaming times as short as 15 sec. The answer would appear to be that sodium hydrosulphite in presence of caustic soda at the elevated temperature of the "flash" ager shortens in an almost unbelievable manner the time for dye reduction, whereas techniques based on potash-Formosul are apparently handicapped by the greater stability of the Formosul at relatively high temperatures. Quite obviously, here is a fruitful field for study using the percentage dye fixation method of assessment. A little work on the pad-steam method as practised in

England has been completed in time for presentation in this paper, but no results are available at present to enable a direct comparison of the merits of the two processes to be made.

EXPERIMENTAL

A range of eight dyes has been examined under the following conditions—

(a) The Formosul content of the padding liquor was varied from 0 to 16% with steaming times of 8 and 20 min.

(b) With a standard padding liquor containing—

10 g.	...	Formosul
10 g.	...	Potassium carbonate
20 g.	...	Sodium chloride

Made up to 100 c.c. with Water

for all dyes, the prints were steamed for 0–40 min. in order to determine the rate of fixation

(c) With the standard pad liquor and a steaming time chosen from the results obtained under (b), prints of the dyes at a range of depths were evaluated in order to assess the building-up properties.

RESULTS

The graphs obtained from these experiments were not as satisfactory as those from the normal alkali-metal carbonate-Formosul process, mainly owing to the difficulty of obtaining accurately reproducible padding conditions for small patterns. However, with due allowance made for this, it was possible to establish a fairly close parallel between the behaviour of the dyes under the conditions pertaining to the two processes.

There is a general improvement in Formosul sensitivity for all the dyes examined compared with the conventional process. The graphs obtained for Caledon Printing Jade Green XBN and Caledon Brown R are shown in Fig. 36 and 37. Nevertheless,

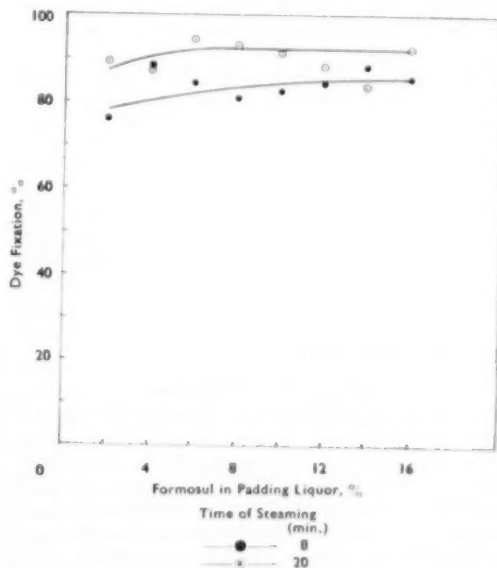


Fig. 36—5% Caledon Printing Jade Green XBN8 Paste, Pad-Steam Process

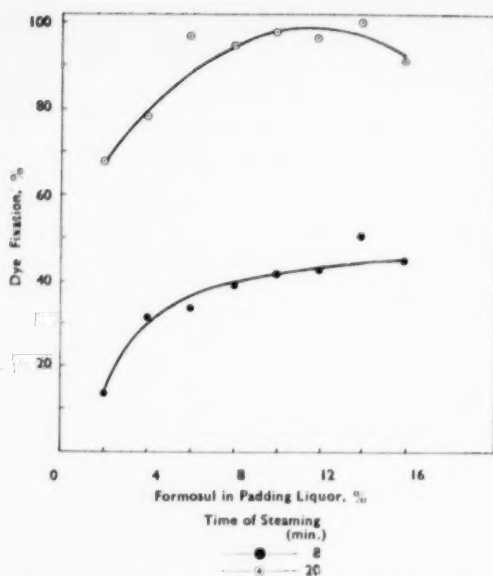


FIG. 37—15% Caledon Brown RS Paste Fine, Pad-Steam Process

although the range of variations is restricted, the general order remains the same, so that the most satisfactory dyes under the conventional process conditions are the most satisfactory by the pad-steam technique, and the same is true for the least satisfactory dyes.

The rate of fixation is similar for the same dye applied by the two processes, with a very slight advantage in favour of the potassium carbonate-Formosul process. This is probably attributable to the fact that there is immediate contact between the dye and the reducing agent in this process, whereas in the pad-steam process some time will be required for the diffusion of the reducing agent and the alkali through the printing thickening to the dye.

The building-up properties show less obvious agreement, and dyes such as Caledon Printing Red BN and Durindone Printing Brown G have markedly superior building-up properties when applied by the pad-steam process. There are, however, differences between this and the work described above on the potassium carbonate-Formosul process, for, as it was desired to adhere to practical conditions, a standard padding liquor was used with no variations to suit particular dyes. In addition, the steaming time was longer for most dyes than that used in the examination of the potassium carbonate-Formosul process.

Discussion of Results

It will be appreciated that this type of study is very time-consuming, and that each of the graphs shown involved the expenditure of considerable effort. As a result, the work is at present far from complete. For example, it is restricted almost exclusively to one fibre, viz. mercerised cotton.

Nevertheless, the results now available have given a clearer understanding of the problems associated with the application to printing of vat dyes.

It has been shown that many vat dyes, which are not normally regarded as satisfactory for printing, could in fact be printed if the conditions could be adjusted to avoid loss of Formosul from the print prior to steaming. In certain cases the limits are so stringent that normal bulk working is impossible, but the advantage arising from the use of specially modified techniques, which have been employed to apply these "difficult" dyes in cases where their fastness properties render their use essential, has been clearly demonstrated.

The approach used has also enabled data to be obtained which the earlier comparative methods failed to disclose. Thus the maximum-fixation data now available indicate that with many dyes it should be possible to increase the amount of dye fixed to the fabric by modification of either dyes or processes. Again, the destruction of dye which occurs with the Durindone types during steaming has opened up another field for investigation, which earlier methods of visual assessment did not reveal.

Future Prospects

In conclusion, it may be helpful to outline how future experiments are being planned to breach the obvious gaps in the fabric of this investigation.

Frequent reference has been made throughout to Formosul sensitivity, particularly lack of Formosul in the printing paste, to which the majority of vat dyes are sensitive. The average printer sets up his formulations with a reasonable excess. Where does it go? Quite clearly poor yields, usually manifest as gross unevenness in the printed piece, indicate that the Formosul was not there when required in the steamer, and the well known expedient of repadding the pieces so affected in Formosul proves its deficiency, if proof indeed were needed. A check on the Formosul content of the prints throughout all stages of processing might be revealing, the technique for such checking having already been provided by Specht¹¹. To date we have employed this iodine titration method only to ensure that under our laboratory conditions the losses of Formosul from the prints were negligible, so that the Formosul introduced into the print pastes corresponded to that present on the prints as they entered the steamer.

Commercial vat dyes, which have been used in all the experimental work, are not necessarily simple dispersions of vat dyes in water, and may contain small quantities of other substances designed to influence their physical condition and ease or rate of fixation. In consequence, under adverse conditions of storage prior to steaming one printed fabric may be affected with regard to Formosul concentration differently from another.

Such discussions inevitably lead to the vexed and little understood subject of optimum particle size for vat-dye printing pastes. Again it must be admitted that very incomplete and inconclusive information exists. Insufficient milling will immediately reveal itself in practice by the production of "specky" pale-shade prints, but there appears no real evidence that particle size is a major factor in determining ultimate printing efficiency. This statement must, however, be limited by the proviso

that no serious attempt has yet been made to study the subject by means of the techniques described in the present paper, although some work on the influence of particle size on rate of reduction has been described by Marshall and Peters⁴.

Finally, it is felt that a careful study by the present technique of adverse steaming conditions created by deliberately introducing superheated steam, air contamination, excess formaldehyde fouling, and inadequate steam supplies would yield valuable results.

With this mass of data available, it should then be possible to direct research towards the manufacture of commercial vat-dye pastes with better printing characteristics and towards new and better techniques of application. The third possibility is the discovery of a new and perfect reducing agent, stable under presteaming conditions but releasing its available hydrogen at about 101°C. It is indeed remarkable that since the discovery of sodium formaldehyde-sulphoxylate almost fifty years ago no product has yet surpassed it, although there are signs in the U.S.A. that it may yet be superseded by sodium hydrosulphite, the compound it once replaced to become the virtual foundation stone of vat-dye printing techniques.

* * *

The authors would like to record their appreciation of the services of Mr. W. F. Liqueurice and

Mr. F. R. Alsberg, who not only have carried out the experimental work but also have prepared the graphs and have contributed to the original thought required to devise the varied experimental procedures.

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Discussion

Mr. J. W. RUWHOF: (1) What a printer wants is not only to get as much dye-fixation, but also to get as much colour as possible⁵. Is it your intention also to study this aspect of printing efficiency?

(2) The speed of fixation is dependent on quite a lot of factors. Does the difference in the rate of fixation stay under varying conditions (e.g. composition of printing paste)?

(3) I was quite amazed to see that the thickener composition did not affect the ultimate fixation, comparing this with what Myers and Turner state in their paper. Is there any explanation for this?

Mr. R. THORNTON: (1) Initially we have concerned ourselves with the absolute efficiency of the vat printing operation but it will be noted that the change of thickening does not seriously interfere with the yield measured in this way. It is true that the economic considerations of industrial practice are more concerned with visual efficiency but there are conditions of cloth, engraving, design and style which dictate that some visual efficiency must be lost to obtain a given technical or artistic effect. We believe the graphs in Fig. 26-27 adequately illustrate that chemical efficiency is well maintained under widely varying physical conditions. With regard to (3), which is inter-related with (1), it appears from our experiments that of the three factors involved in vat printing namely—

- (a) rate of reduction of the vat dye
- (b) sensitivity of the vat dye to Formosul concentration
- (c) rate of transfer of the leuco dye from the thickening into the fine structure of the fibre

(a) and (b) are the dominant ones and (c) is relatively unimportant.

With regard to (2) the speed of fixation under a given set of conditions can be influenced profoundly in the steaming time range of 1-5 min. by compounds which themselves have an electro-negative potential and which therefore would appear to act as reduction catalysts.

Mr. E. FREDMAN: Have your steaming conditions been comparable with industrial steaming, or how do you characterise them?

Mr. THORNTON: It can be said that the laboratory steaming conditions used throughout these studies are superior to those which would normally be found in practice in that the steam is air free, fully saturated and free from superheat. Furthermore the working pressure in the ager is such that for all practical purposes the temperature is maintained at 100-101°C. and temperature rise in the ager, usually attributed to the exothermic heat of solution of potassium carbonate, never takes place as the ratio of weight of printed cloth to total volume (or weight) of steam does not allow this effect to manifest itself.

It is realised that a study of non-perfect steaming conditions approximately to normal industrial conditions would repay study, therefore work is planned to this end. All safeguards in steaming conditions designed to maintain air-free, saturated nonsuperheated steam at 100°C. have the object of preventing premature decomposition of Formosul rather than degradation of the leuco vat dyestuff itself.

Dr. W. SHAW: It has been stated that the reason for the enormously increased speed of fixation obtainable by means of the "flash steam" method in comparison with the potassium carbonate-Formosul pad-steam method is the much shorter time required for reduction of the dye in the former case. This does not appear to be a complete explanation however, as W. G. Marshall and R. H. Peters (this Symposium) have shown that vat dyes, applied by an "all-in" method, have times of fixation exceeding those needed for reduction by 150-770 sec. This is presumably true in the case of the potassium carbonate-Formosul pad-steam process also since the rates of fixation are very similar for the two processes. Is it yet known why the time of transfer of the reduced dye from the paste to the fibre should be so shortened by the use of the "flash steam" method?

Mr. THORNTON: Before any well substantiated opinions can be held about the so called "flash steam" process it will be necessary to study a series of characteristic vat dyes on laboratory scale equipment under conditions approximating to full scale "flash" operation but strictly comparable to the conditions outlined in this paper with regard to the control of the mechanical printing operation and the ultimate optical estimation of efficiency.

Such work is to be done. In the meantime, in part answer to the query it should be pointed out that the "flash" method uses a caustic soda-hydrosulphite powder reducing system with an average electro-negative potential of -1150 mv. against the so called "all in" and "pad-steam" processes which normally use a Formosul-soda ash or potash reducing system with an average electro-negative potential of -900 mv. One would expect a more electro-negative potential coupled with the fact that reduction begins *at once* in the padding stage to increase the speed of reduction considerably.

On the other hand it should be remembered that the presence of caustic could be expected to bring about a greater swelling action than an alkali carbonate and such a system with a lower electrolyte content may promote a greater degree of molecular dispersion of the leuco vat dye. Finally "flash" methods are characterised by very low solid content thickenings and here again one would expect a higher migration speed.

Some evidence for these views is forthcoming from considerations of the Standfast molten metal process where the dyeing time in absence of any thickening is in the region of 3 sec.

Mr. E. B. CROSLAND: Is any work proposed on the printing efficiency of mixtures? For example, Caledon Printing Purple 4RS and Caledon Blue GCPS show different Formosul sensitivity curves, but they are widely used together in mixtures. Can the lecturer offer any guidance to the works chemist?

Mr. THORNTON: Work on mixtures would certainly repay study and the results may not of necessity represent a mean of the behaviour of the components since some one vat dye may or may not

act as a reduction catalyst for the others in the mixture.

As the question points out a two colour mixture of Caledon Printing Purple 4RS and Caledon Printing Blue GCPS entails a compromise where some efficiency of the purple component has to be sacrificed to ensure that the blue component is not over-reduced.

Practically, investigational work to study these problems will be handicapped by the difficulty of measuring absorptiometric strengths of the resultant mixture extracts.

Mr. J. H. FLEMING*: Mr. Thornton in presenting this paper said— "Having presented the dye to the fibre, you then have a series of complicated processes such as steaming." This statement bridges a very wide gap, in which we have such factors as drying conditions on the printing machine (which can vary between wide limits), the storing of the printed pieces prior to steaming in an atmosphere varying in temperature and relative humidity.

Now it is quite obvious that the authors had something in mind regarding this vital period, for they state in the preprint of their contribution: Frequent reference has been made throughout to Formosul sensitivity— particularly lack of Formosul in the printing paste, to which the majority of vat dyes are sensitive. The average printer sets up his formulations with a reasonable excess. Where does it go?

Mr. THORNTON*: It is perhaps not generally appreciated—

(a) how quickly or to what extent Formosul decomposes under the influence of steam

(b) the number of factors which influence the rate of degradation of Formosul when a typical print formulation is being dried or stored.

This paper demonstrates that under well controlled conditions printing efficiency falls rapidly as the Formosul content of the printing paste decreases. It should, however, be remembered that all the prints used in these efficiency estimations were handled in such a way that the Formosul content shown on the graph was in fact the correct figure and to this end frequent checks by analysis have been made. With regard to (a) initial studies indicate that 50% of the total Formosul may be decomposed in 3 min. with a typical vat dyestuff in British Gum thickening. Thus any conditions in print drying which approximate to steaming conditions as can easily occur with badly ventilated entering ends of drying ranges or hot flues can speedily cause the Formosul content to fall to a dangerous level before any true fixation can be effected.

In connection with (b) it can be said that increasing temperature, especially at temperatures above 120°C ., moisture, caustic alkali in place of potash, The effect of certain metallic salts notably iron and the use of some low solid content thickenings are all factors which increase the speed at which Formosul is decomposed.

The subject is too large and our initial experiments too incomplete to prove the foregoing in a conclusive manner but the following selected

examples based on experiment all point to the necessity for care between the mechanical operation of printing a typical vat dye formulation and the steaming operation.

(i) Drying: A wet print loses about 14% Formosul in one hour at air temperature whereas a carefully air-dried print (70°C.) loses only 5.5% Formosul. The average loss of Formosul when drying between temperatures 70–105°C. is in the order of 10–20%. If the temperature is raised to 120°C. it may under adverse conditions lose 30% whereas under the same adverse conditions a loss of 65% may be realised.

(ii) Storage: In 24 hours one can expect to lose a further 10% Formosul on the assumption that the initial average loss due to controlled drying was in the order of 10–20%. In 48 hours with some dye-stuffs a total loss of Formosul amounting to 50% may be experienced.

(iii) Steaming: Approximately only 30% of the Formosul remains in the print after 5 min. steam and the residue may be as low as 4% of the initial concentration after 20 min. steaming.

(iv) Formosul concentration: The initial rate of decomposition of Formosul under adverse conditions (i.e. steaming) is greater with a low concentration than with a high concentration.

It must be stressed that these findings are very approximate averages but it is thought they serve to illustrate how readily under adverse industrial conditions the Formosul content of a vat print is affected.

Mr. S. G. CORBISHLEY*: With reference to the finding of Marshall and Peters, that the rate at which a dye fixes must therefore depend on its rate of reduction and in general, dyes with low rates of reduction will require longer times of fixation, we wish also to refer generally to the paper of Michie and Thornton, which draws the conclusion that the

Formosul content of the printing paste is the most significant factor in the rate of fixation and final yield of the dye on the fibre.

Will the authors reconcile these conclusions with results obtained by printing vat colours by the prereduction method, i.e. the vat dye is completely reduced in the thickening by warming with caustic soda and hydrosulphite of soda at 140°F. for a period of 15–30 min. The free caustic alkali is then neutralised with sodium bicarbonate.

It has been observed that the times of fixation of vat dyes printed by this method are substantially the same as when printed by the more usual carbonate of potash method, and that individual dyes show identical fixation properties. Progressive fixation and yield is obtained exactly as shown by Michie and Thornton up to times of 16–20 min.

This would seem to indicate that the rate of reduction of the dye has no fundamental bearing on the rate of fixation and final yield of dye on the fibre.

Mr. THORNTON*: No measurements of fixation using the methods outlined by Michie and Thornton have been as yet made with formulations based on prereduction recipes but some studies using vat dyes with known low rates of reduction isolated as experimental leuco compounds have confirmed that speedier fixation is thereby possible. It does appear from the latter part of the question that yields based on steaming times of the order of 16–20 min. are under review. In this case the practical effect of the actual time of reduction of the vat dye is so small a proportion of the total time of steaming that its effect is lost. When, however, short steaming times are practised and equilibrium conditions are not reached the effect of prereduction, i.e. the elimination of the reduction period from the migration or dyeing period is evidenced in the yield of the print. Such steaming times range from 1 to 5 min.

* Communicated

Dye Transfer in Dyeing and Printing

G. D. MYERS and H. A. TURNER

The results obtained in the study of dye transfer from thickener to fibre-substance, during steaming, for a number of different classes of dyes, have been compared with the results of parallel work on dyeing in order to demonstrate the essential similarity of the two methods of coloration.

The steaming process in textile printing has two major functions, the relative importance of which may vary from one printing style to another. They are—(a) to provide favourable conditions for the transfer of a dye or a dye-generating substance (including dyes which have undergone a reversible chemical change, principally to render them water-soluble) to the fibre-substance from the printing paste applied from roller, screen, or block; (b) to bring about reactions which will transform a normally non-diffusible dye into a diffusible form (e.g. in most styles for the printing of vat dyes) or which will convert a diffusible into a non-diffusible form once the transfer has been accomplished (e.g. in many mordant styles).

Since the dyes used in printing are mostly those which are used in dyeing, and since the condition and the distribution of these dyes in the textile fibres of a finished printed fabric are not usually different from the corresponding condition and distribution in a finished dyeing, the fundamental mechanisms of dye transfer are likely to be very similar in the two methods of textile coloration. In detail, however, there are obvious and important differences. These generally make printing methods and printed goods more difficult to examine by quantitative methods than dyeing methods and the resulting dyed materials in which the same dyes are used. This accounts for the much greater attention given to dyeing than to printing in the fundamental studies of dye transfer which have played so large a part in modern textile technology. But the disparity should not be over-emphasised. Studies of dyeing mechanisms are, even now, far from complete, and the extent of progress varies from one dyeing system to another. The "easy" systems—easy for laboratory investigation, that is—such as those which include the direct cotton dyes and regenerated cellulose fibres, have been explored much more fully than uncommon or complicated ones. For the satisfactory industrial progress of printing it is essential that a very great deal should be known about the chemical reactions of the dyes which are being used, and the abundance of "colouristic" knowledge may fairly be held to compensate for the relative paucity of "transfer" knowledge.

Since 1948, studies in this Department have been directed to the development of a more accurate understanding of the processes of dye transfer in printing systems during the steaming process. The complexity of actual printing systems has caused the experiments to be made with laboratory models which differ in many secondary details from those of a representative print, and, although much work has been done, much more will be needed before it is possible to apply the laboratory

results consistently and effectively to the control or development of actual printing processes. In this work, attention has been focussed upon the steaming process as it is employed to encourage dye transfer from the imposed printing paste to the fibre. Only when necessary for a complete understanding of the primary purpose has attention been given to the second function of steaming, viz. the promotion of chemical reactions.

Thus, the observations that have been made, and the conclusions that have been drawn, have related to stages in the complete production of printed goods which correspond to those stages in the production of dyed goods in which the dye is made to enter the fibre—the dyeing process proper—and have less resemblance to stages in which the textile material or the dye are being prepared for dyeing, or in which the dyed material is being aftertreated.

INVESTIGATIONS OF DYEING PROCESSES

Of recent years, there have been many accounts of investigations of dyeing processes, and a number of useful summaries have been given. The Dyeing Symposium of 1947¹ brought together many aspects of this kind of work, and it was followed by publication of *The Physical Chemistry of Dyeing* by Vickerstaff², which, insofar as the principles of dyeing processes are concerned, will be regarded as authoritative for some time to come. It is unnecessary, therefore, to discuss these principles here at great length, but in order that the comparison between dyeing and printing processes may be sustained, some brief attention must first be given to dyeing. As pointed out by many previous authors, dyeing has been studied for the most part in one of two ways—kinetically, by following the course of dye translocation, and statically, by interpreting the significance of the proportion of dye taken up when the system has reached an equilibrium state.

When it comes to application of the results of theoretical studies to industrial dyeing processes, it will be seen that the kinetic approach may be expected to give information which will allow the course of dyeing to be more accurately controlled and will be immediately useful in the dyeing operations themselves. The second approach will help to define the properties of the dyed goods, and so will interest the user as well as the dyer. Theoretically, the first kind of studies must start with a mechanical picture of diffusion processes, the movement of dye particles of defined size, shape, speed, and density of distribution through microporous fibres also of a defined constitution and structure. The second approach is concerned chiefly with the limitation of freedom of these

particles once they are within the fibre, such limitation being brought about either by chemical forces operating between parts of the dye molecule and parts of the fibre molecule or by aggregation of dye molecules to particles so large that they become entrapped in the fibre structure. The one set of factors—those which govern fixation of dye—influence the operation of the others—those which govern diffusion—and the greatest triumphs of modern dyeing theory are seen in work which has achieved a connection between the two.

In investigations of dyeing processes in the form in which they are most amenable to theoretical treatment, reproductions on the laboratory scale for the purposes of quantitative measurement have nearly always followed those dyeing processes which work with a high liquor: goods ratio, and in which the circulation of the liquor relative to the goods is not specially directed. In fact, the earlier work was done, with the object of making the results easy to interpret, with the so-called infinite bath, i.e. with a ratio so large that the concentration of the bath did not change measurably during the course of the dyeing experiment. This choice excluded dye application by padding, an operation which is, in many particulars, *sui generis*, and is very interesting when dyeing and printing are being compared. It is encouraging to find that this process is now in prospect of being studied much more thoroughly.

With the exception of work on solvent and "carrier" dyeing for the so-called hydrophobic fibres and also, perhaps, of recent work on high-temperature dyeing, theoretical investigations have seemed to be much more concerned with the description and the understanding of traditional dyeing methods than with the development of radically new ones. This is true even when processes are required for the new synthetic fibres, which differ from the older fibres in many of their dyeing properties, the older dyes and the older methods being adapted, rather than new products and methods of application being devised.

FACTORS IN DYE TRANSFER

The diffusion of gases or of dissolved particles has been defined in Fick's law as a linear relation between the rate of passage dS/dt of the particles through a fixed area perpendicular to their path and the local concentration gradient dc/dx along the path of diffusion—

$$\frac{dS}{dt} = -D \frac{dc}{dx}$$

(D = coefficient of diffusion). This equation might well describe the behaviour of the dye in the dye-bath, on its passage to the fibre, but the dyeing system as a whole is heterogeneous, and some modification of the simple equation will be needed. In dyeing, the importance of concentration gradients in the bath is generally small, because stirring or other means of circulation tends to eliminate them. The dye is carried to the fibre in moving solution, and only in a region very close to the fibre surface does stirring become ineffective. Then diffusion through quiescent liquid has to

be relied upon to provide dye steadily for the fibre. Although this layer is thin, it has a measurable effect on the rate of dye uptake, for this rate can be augmented appreciably by more vigorous displacement of the dyebath liquor. The approach of a dye particle to the surface of the fibre may suffer a restriction if it should carry a negative ionic charge, as so many varieties of dye particles do. This has been shown, by Neale³ especially, to be due either to electrical repulsion by the negatively charged fibre surface, or to a local concentration of the positively charged gegenions of the adsorbed dye. There is thus a region just outside the fibre where dye transport has the characteristics neither of diffusion in the bath nor of diffusion within the fibre.

There is still much to be learnt about diffusion within the fibre. It can be followed quantitatively by examining cross-sections of fibres removed at intervals from the bath during dyeing. With many substantive dyes, and with a number of different textile fibres, this examination reveals in the early stages the phenomenon of "ring-dyeing". During a short initial period, a considerable proportion of the dye present enters the fibre, and remains concentrated in a narrow peripheral zone. From this zone, dye diffuses more slowly, if dyeing is continued, towards the centre of the fibre. This is the process which has most interested the investigators. Practically all of them, in attempting to measure dye diffusion within the fibre, have taken the high concentration in this ring region as the datum from which concentration gradients, which cause the diffusion, first start. It is probable that this ring was first assumed, for theoretical purposes, before its presence was actually demonstrated. If an initial equilibrium is set up very rapidly between the concentration of dye in the bath as a whole and the concentration in the ring region, and if the experimental conditions correspond to the maintenance of an "infinite" bath, then the dye diffusing within the fibre must always start from a region of constant concentration. However, when the dyeing is done in a way which corresponds more nearly to practical dyeing, and the dyebath becomes exhausted during the operation, it still appears, from calculations made by Crank⁴, that the concentration in the ring must remain constant, at the value which it first attains, and independent of subsequent changes in the bath. This deduction should be borne in mind, for, as will be seen later, it may apply also to printing systems.

When the dyeing process has not reached equilibrium conditions, the dye may be present within the fibre in a wide range of local concentrations, from the high values prevailing in the "ring" to zero at the centre. There has been no effective direct measurement of diffusion over any interval of this range, as it is actually taking place within the fibre. The nearest experimental approach has been the work of Garvie and Neale⁵ with packs of Cellophane, dyed together and afterwards separated for examination, and of Boulton and Morton⁶, who studied the diffusion of dye in the plane of the cellulose sheet. For the most part, however, measurements have consisted of determinations of

the partition of the dye between the dyebath as a whole and the fibre-substance as a whole at intervals during the course of the dyeing. It has thus been necessary to postulate some rule, most conveniently in the form of a differential equation, which would relate the constantly changing concentration of dye in some very small volume of the fibre with the constantly changing difference in concentration around the same volume. This equation, when integrated between suitable limits of time and of distance along the path of diffusion, will give the total dye transfer to be expected between bath and fibre, and this can be compared with the measured transfer as a test of the validity of the proposed equation. This is, of course, a well established procedure in this field, and several equations have been tested in this way. It is mentioned again here to emphasise the desirability of finding an experimental method for the direct instead of the deduced construction of a diffusion law applicable to a particular dyeing system. It will later be seen that the desirability is even greater with printing systems.

Where the dye molecules can be imagined to diffuse, with nothing more than mechanical restrictions, in water which has entered the pore system of the fibre, Fick's law suitably adjusted to meet the special geometry of the system might represent the behaviour of the dye. With substantive dyes, however, the movement of dye particles is not wholly controlled by local differences in concentration. Where the distance of separation is sufficiently small, chemical forces operate between the dye molecules or ions and the molecules or ionic groups in the solid network which forms the fibre-substance. Sometimes, e.g. with a direct cotton dye and a cellulosic fibre, this separation has to be very small, but sometimes, as with wool and an acid dye in an acid bath, every dye particle within the fibre, and some outside it, may be considered to be under the influence of chemical forces emanating from the fibre-substance. Thus, according to the kind of chemical force and the distance of separation, the diffusing molecules are slowed down, either suffering a drag from the walls of the pores, or being attached and immobilised on these walls for greater or smaller intervals of time during their forward movement. With this diversion for the diffusing particles, there will be a slower dye transfer from point to point within the fibre, under the influence of the same concentration difference, than if the dye particles and the walls were indifferent to each other. The diffusion coefficient will therefore be less in diffusion with adsorption than in pure diffusion. Furthermore, most of the dye molecules that can become attached chemically to the fibre-structure are, by the very chemical constitution which makes this possible, capable of becoming attached to each other. Thus, for some dyes, and for some dyeing conditions, some of the diffusing units are much greater in size than simple dye molecules. This may make them unable, until they break down, to enter into all the pores of the fibre-substance⁷.

It will thus be seen that the diffusion of a dye in a fibre, induced by the same concentration difference,

may vary in a variety of ways if other factors in the environment are made different. Further, a number of these factors are either known or likely to depend on the ambient dye concentration. For instance, when dye molecules are crowded more closely into the pores of the fibre, the proportion which come within the influence of the walls or of each other will be changed also. This has led to a number of enquiries into the change of diffusion coefficient, or of rate of diffusion caused by a standard difference in concentration over a standard distance, which may take place when the local concentration of the dye varies^{5,8,9}. If there is a variation in the diffusion coefficient in this way—a change in the intrinsic capacity for diffusion when the prevailing concentration alters—it will be very important when we are considering the movement of dye in a partly dyed fibre, in which the concentration varies from point to point as we go from the outside towards the centre. Further, if allowance is not made for this effect, it will be impossible to obtain integrated values for dye transfer which may properly be compared with the results of rate-of-dyeing experiments. Most of the enquiries in this field have been concerned with cellulosic fibres and films, and the dyes which are substantive towards them. Most of the suggested relations have been based on the assumption that Fick's law would hold for a dye diffusing without adsorption, so that the "true" diffusion coefficient D_0 , the constant in that equation, is truly constant. Then D_e , the apparent diffusion coefficient obtained from dyeing experiments, will be defined by the general relation—

$$D_e = D_0 f(c)$$

In the dyeing of a pack of cellulose sheets, the variation of diffusion coefficient with concentration has been shown, and variations of D_e directly with c and with \sqrt{c} for direct cotton dyes on cellulose have been recorded^{10,5}. In the work of Boulton and Morton¹¹ the diffusion coefficient is shown first to rise and then to fall as the concentration of accompanying electrolyte is increased. This is not unexpected, for moderate concentrations of salt will tend to free the dye ion from the restraints imposed by other ions in the system, while large concentrations will cause aggregation of the dye.

In printing, it will later be shown that the effect of environment upon diffusion in the fibre-substance may be of very special interest for the following reasons—

(a) The dye may be presented to the fibre in effective concentrations greater than those which normally prevail in the bath during dyeing.

(b) For this reason, the "ring" concentration set up in the fibre, during drying of the print or at the commencement of steaming, may be correspondingly high.

(c) Dyeing can, in general, be accepted as transfer of dye to a fibre-substance fully swollen with water. If deliquescent are absent from the printing paste, it is certain that cellulosic fibres, at least, are not fully swollen during the steaming of a print.

(d) The overall concentration of electrolytes in the water taken up by the thickener layer during steaming, corresponding to the bath in dyeing, may, however, be very high. Unless special measures are taken, the aggregation of the dye at this time may also be very pronounced.

(e) In dyeing, the bath is an aqueous solution. The dye molecules can thus associate only with mobile water molecules, and the rate of diffusion in the bath will be much greater than in the fibre. During steaming, with the bath represented by a water-swollen thickener, the dye will be diffusing to the fibre in a medium which may have to be regarded either as a very viscous liquid¹² or as a structure resembling the fibre-substance in many important respects.

(f) Because the dye may be present at a high concentration in part of the fibre during the steaming of a print, another action, not yet considered very thoroughly, may have to be taken into account. This is that the dye may assist in swelling the fibre-substance, and so in "making room" for itself. The studies of Crank and Park¹³ on the diffusion of solvents into blocks of high-polymer substances may be pertinent here. The analogy may be twofold: the swelling of solid material by diffusing solvent may act as a model either for the progressive swelling of thickener or fibre-substance by water abstracted from steam, or for a process whereby the fibre-substance is further opened up by the first dye molecules to enter, making diffusion easier for later entrants. In Crank and Park's experiments, D remains low for low concentrations of the diffusing substance, but after a critical concentration has been exceeded, it rises rapidly.

(g) There is nothing in the steaming of a print which corresponds to the circulation of the bath, relative to the fibre, in normal dyeing. The distance that the dye has to travel to reach the fibre is, however, very small, and often of the same order of dimensions as the diameter of the fibre.

STEADY-STATE DIFFUSION

When a fibre, or a film of fibre-substance, is immersed completely in a dyebath, the direction of migration of the dye is from the outside towards the centre. The fibre "fills up" with dye, and this imposes a rapidly changing concentration gradient at points within the fibre-substance and finally a stoppage of the diffusion process. Garvie and Neale⁵ used the device of taking the fibre-substance in the form of a film separating a solution of high from a solution of low concentration of the dye, and were thus able to prolong the diffusion process. If the concentrations of the two solutions are maintained substantially constant, a steady state is obtained, in which, after an initial period, the dye diffuses at a steady rate through the film, the concentration of dye at each point remaining constant for as long as there is no further chemical or physical change in the film-substance. This enables diffusion processes to be examined at greater leisure and with greater possibility of changing the controlling factors one at a time. This mechanism has been thoroughly studied by

Barrer¹⁴, and its experimental virtues for the study of dyeing processes have been pointed out by Vickerstaff².

It was thought that this method would be useful in studying the diffusion of dyes from baths approaching in dye concentration the values which prevail in the thickener layer when a print is steamed. In fact, attempts were made by Heritage in this laboratory to get even closer to the conditions of printing by trying to establish steady-state diffusion for a direct cotton dye, Chrysophenine G, in a system which consisted of a cellulose film sandwiched between two similar starch films, in one of which the dye was incorporated, while the other was initially blank. This system was steamed. Manipulative difficulties were considerable, especially in establishing the time of diffusion, but approximately steady conditions could be maintained for some time, although the accuracy was not very high. This work did serve, however, to bring out an important fact about printing with direct cotton dyes, viz. that it is possible for the affinity of dye for the starch thickening to be greater than its affinity for the fibre. This was found, for instance, to be true with Chrysophenine G, while the affinity of Chlorazol Sky Blue FF was greater for cellulose than for starch.

With solutions of purified Chrysophenine G and Cellophane, the steady-state method has brought out two or three other interesting points—

(1) Confirmation that the slow diffusion of the dye in cellulose, as compared with its diffusion in water, is partly due to the mechanical difficulties encountered by the dye particles in getting through the fibre-substance, and is not due wholly to adsorption. This is shown by the relatively small proportion of dye retained by the cellulose as compared with that which can pass through in the course of an experiment, when this is taken in conjunction with the fact that there is a marked osmotic pressure set up on the side of the membrane where the concentrated dye solution is placed (e.g. about 2 cm. of water for salt-free Chrysophenine, 3.0 g./litre at 70°C.).

(2) On the basis of a diffusion equation such as has been discussed, Crank⁴ has constructed rate-of-exhaustion curves for a direct cotton dye from aqueous solution on to regenerated cellulose, firstly assuming that the bath concentration did not change appreciably during the course of the dyeing, and secondly that it did so change, perhaps to 10–30% of its initial value. The hypothetical curves for each of these conditions were then compared with the actual exhaustions obtained when dyeing took place from a bath of restricted volume so that the ultimate concentration of the bath was diminished to the extent mentioned above. It was found that the experimental curve corresponded more closely to the hypothetical "infinite" bath curve than to the one for the "finite" bath. This effect has not yet been fully or satisfactorily explained, but it leads to speculations as to whether the concentration of dye in the ring zone can be determined by the initial concentration of dye in the bath, and cannot then be altered by any

subsequent changes in dyebath concentration. In other words, the pattern of diffusion into the fibre is determined by conditions which exist only at the beginning of the dyeing operation. This supposition can be disproved experimentally in the diffusion apparatus. An experiment is started and allowed to continue until dye passes through the cellulose film at a steady rate. The concentration of dye in the solution from which diffusion is taking place is then suddenly diminished. Within two or three minutes, the time normally required at the beginning for Chrysophenine G to pass through the film, there is a rapid fall in the rate of transfer of dye to the other side of the film.

(3) The relation between dye concentration and apparent diffusion coefficient is shown, for steady-state experiments, in Fig. 1, which refers to

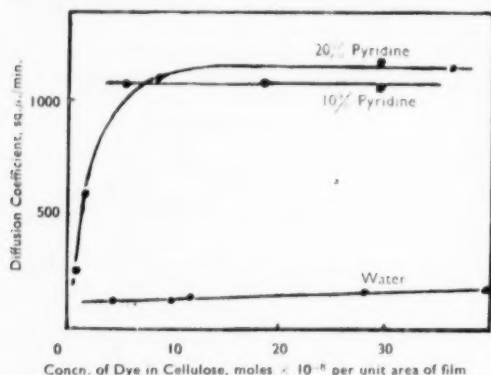


FIG. 1—Change of Diffusion Coefficient of Chrysophenine G with Concentration in Cellophane, for Water and Pyridine-Water Solutions

Chrysophenine G solutions at 70°C. in water and in 20% aqueous pyridine. These experiments confirm that the rate of diffusion of this dye through cellulose is relatively small and that the coefficient, estimated for the complete thickness of the film, increases linearly with increasing initial concentration, confirming the suggestions of Crank. The addition of pyridine is seen to increase the diffusion coefficient very greatly, and, except for the most dilute solutions in the series, is also shown to make it almost independent of concentration. Since Standing *et al.*¹⁵ have shown that this dye does not aggregate readily at the temperature of the experiment, it is possible that the pyridine has depressed adsorption of dye by the cellulose, and that the behaviour of the system has approached that of one in which diffusion takes place without adsorption. In a system of this kind, as we have seen, the apparent diffusion coefficients will approach the values of the corresponding true diffusion coefficients, and are expected to be more nearly independent of concentration.

DIFFUSION IN PRINTING SYSTEMS

Most of the information on printing systems which is available for discussion has come from dye-transfer experiments in which the normal printing system has been imitated by bringing a dried film of thickening agent containing the dye into contact with a film of the fibre-substance, steaming the two

together, and then estimating the dye present in each film. The technique has been described a number of times. In the earliest experiments, Munshi and Turner¹⁶ showed that, for purified Chlorazol Sky Blue FF (ICI), neither the initial rate of transfer from starch to cellulose, nor the proportion of dye transferred at equilibrium, could be related simply to the initial concentration of dye in the starch. This has inspired a closer examination of the relation between diffusion coefficient of dye in the cellulose, under printing conditions of transfer, and the concentration of the dye, with results that will be described later.

Although not expressed in terms of diffusion coefficients, a change in the chemical constitution of the thickening agent was found, not unexpectedly, to be capable of causing substantial changes both in the rate of transfer to the cellulose and also in the ultimate exhaustion of the dye. This general observation has been made with a number of different dye classes¹⁷⁻²⁰. The effects are certainly complex, and among the factors operating are probably—(a) the capacity of the thickening agent to take up water from the steam, (b) the structure of the swollen film of thickener, (c) the kind and the frequency of chemical bonds between the dye and the thickening agent. One very pronounced effect is that observed when thickening agents containing a large proportion of ionising groups (e.g. sodium alginate and starch carboxyethers) are used with dyes (acid, direct, and Indigosol) which can furnish dye ions with the same electrical charge. Here the rate of transfer to the fibre-substance is generally very rapid, and the ultimate exhaustion high, so that it seems reasonable to suppose that the dye ions are being accelerated by electrical repulsion in their passage from the thickener to the fibre, and that, in a reversible transfer, the return passage from the fibre to the thickener is being retarded.

It has been suggested that, since the movement of dye from the thickener and into the fibre is, in part, a reflection of the diffusion coefficients in the thickener and in the fibre respectively, it is likely to be more rapid when the dye particles are not strongly attracted by the main constituents of either phase, so that there is diffusion without adsorption. This has been demonstrated by the extraordinary mobility of certain acid dyes in a model starch-cellulose printing system. With a simple, readily soluble dye like Naphthalene Scarlet R (ICI), very substantial transfer to, and penetration into, cellulose can occur in the cold. This was demonstrated by Patel¹⁸ during the drying down of the printing paste in contact with the cellulose, for he found that dye moved consistently into the cellulose film until so much water had been removed that diffusion stopped altogether. The amount of water necessary for diffusion is not, however, very large for dyes of this kind, as has been shown recently by W. K. Birtwistle of the Calico Printers' Association Ltd. In ordinary film-to-film experiments with the dye Solochrome Red B (ICI), he has found that, when the dry dye-containing starch film is brought into contact with water-soaked Cellophane in the cold, appreciable

transfer may at once be detected. This continues, and after 20 hr. almost 30% of the dye has passed to the cellulose.

These soluble acid dyes behaved peculiarly in another respect in that the net direction of dye transfer during steaming could be reversed; i.e. the dye would go first from starch to cellulose and then, after a while, from cellulose to starch. This effect has been investigated a great deal, first by Patel¹⁸, and later by Pomfret²¹ and by Dastur²³. It seems to have no counterpart in normal dyeing experience, unless a somewhat remote connection with the levelling behaviour of certain direct and leuco vat dyes is imagined. A satisfactory explanation, which will apply reasonably well to all the idiosyncrasies of these acid dyes during their migration towards cellulose, has not yet been obtained. We have been led by these observations to consider one very important difference between typical printing systems and typical dyeing systems. In dyeing experiments, as they are usually performed in the laboratory, the volume of the dye-bath remains constant. After a very short initial period necessary for swelling, and disregarding later small changes due to the maintenance of the bath at high temperatures, the receptive volume of the fibre changes very little. Thus, any local changes in dye concentration within the system during the course of dyeing are brought about by the movement of the dye itself. In other words, the system in dyeing may be considered to be made up of phases whose spatial dimensions do not vary, and the characteristics of diffusion at any time result from a dye distribution which has come about only as a result of the diffusion which has preceded it. In printing there is a manifest difference, because here there is evidence to show that the dimensions of each phase change during steaming both absolutely and, more important, relatively to each other. We are still unable to investigate these changes directly when one phase is in contact with the other, but Pomfret²¹ has measured the uptake of water by each of the isolated films when suspended in steam. Briefly summarised, his results show that starch takes up moisture readily when first introduced into the steam, and then regularly increases in weight as the steaming continues. If salt is present, the water-uptake is much greater. The cellulose also takes up water continuously during a prolonged steaming, but the uptake is less than with the starch. When the two phases are steamed together, the discrepancy between the water uptakes of the two may be even greater, because there is qualitative evidence to show that the starch may rob the cellulose of some of its share of water. Some experimental results are reproduced in Fig. 2. The net result of all this is equivalent to a dyeing experiment in which the dye-bath is continually being made larger in volume by the addition of water during the course of the experiment. Thus the moment-to-moment distribution of dye concentration as between one phase and another, and also within each phase, is being changed by an agency other than the migration of the dye itself. This agency may be so powerful in its effect that

it may explain the reverse movement of acid dye particles, which, having little affinity for cellulose, can migrate easily to wherever the concentration is lowest.

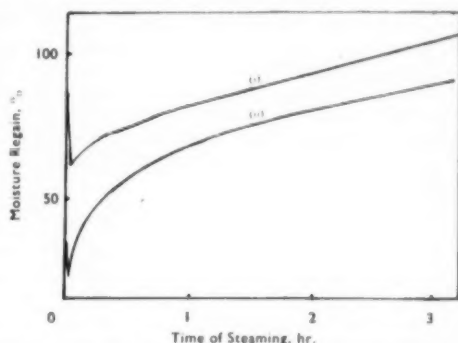


FIG. 2—Moisture Uptake in Steam by (i) Water-soaked Cellulose Sheet, (ii) Starch Film initially conditioned at 75% R.H.

The possibility of reverse dye migration, from the fibre-substance to the thickener, is also seen with the sulphuric esters of leuco vat dyes. In specific examples, two maxima have been found in the dye-transfer curve obtained during steaming, and this points to a higher degree of complexity in the system. It has been suggested that the transfer of the dye is interfered with by chemical changes in the ester, leading to products which are more insoluble and tending towards molecular aggregation and larger migrating particles, which have rates of transfer different from those of the original dye.

This mention of aggregation emphasises a difference, in degree, perhaps, rather than in kind, between dyeing and printing systems. In the latter, the "dye-bath" is so small that the concentration of dye must be correspondingly great, and the amount of dye present must often exceed the solubility. This is, of course, recognised in the formulation of many printing pastes by the inclusion of solvents and dispersing agents. If these are absent, and much of the dye is highly aggregated, quite new diffusion behaviour is to be expected.

One further difference between dyeing and printing systems may be mentioned. A film of thickener imposed upon a textile material has two sides, one represented by the surface of contact with the material, the other exposed to the air or to the vapour in the steamer. With some of the acid dyes we have obtained evidence that dye can migrate, during steaming, to the free side of the thickener layer and can form concentrated films there. It may be argued that a dye-bath also has a surface open to the atmosphere, but in comparison with the surface area of the material being dyed, it is small, and is, in any case, continually disturbed by circulation processes.

After this general discussion of diffusion in dyeing and printing systems, a few detailed examples may now be given.

CRITICAL EVIDENCE OF DYEING BEHAVIOUR

In any attempt to demonstrate the essential similarity of dyeing and printing processes for a

specific dye, the comparison is likely to be most fruitful and to have the greatest industrial significance when the dye chosen has a well marked affinity for the fibre-substance. If this affinity is absent, and restriction on the diffusion of dye is not very great, then the formal instability of the printing system—the liability of each phase to change its size during drying and steaming—is likely to call for many complicated adjustments to the basic diffusion equations before true comparisons can result. This lesson has been learned very thoroughly in studies of the acid dyes applied by printing to cellulose.

Crank⁴ has attempted to find a general diffusion equation for the dyeing of substantive dyes, and one which would apply not only to the more academic conditions imposed experimentally by the use of the "infinite bath", but also to the more practical conditions in which the bath is substantially exhausted during the course of dyeing. A suitable value for the apparent diffusion coefficient is assumed, this value being further supposed to remain constant and independent of concentration. A value is also assumed for the exhaustion of the bath when equilibrium is reached. From these a curve is plotted relating exhaustion with time ($\log_{10} t$) as in Fig. 3.² A comparable curve for dyeing in which the original concentration of the bath remains unchanged throughout can also be constructed using Hill's equation²². The experimental results of appropriate dyeing operations can be graphed in the same way. This analysis was applied by Crank to the dyeing of three direct cotton dyes on cellulose sheet, with the result that, although exhaustion of the bath reached 90%,

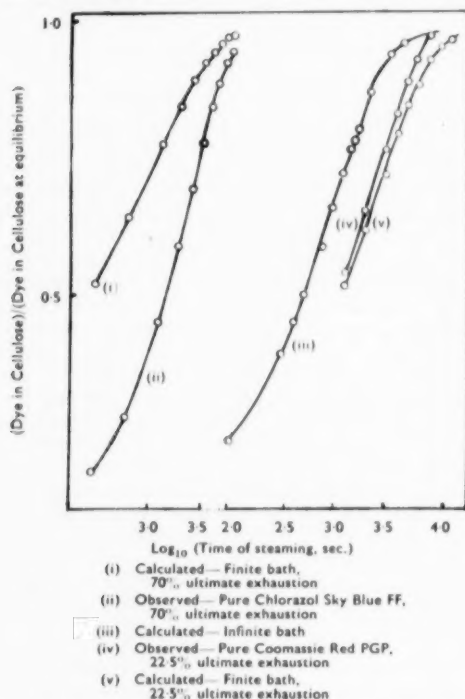


FIG. 3.—Observed and Calculated Dye Transfers during Steaming

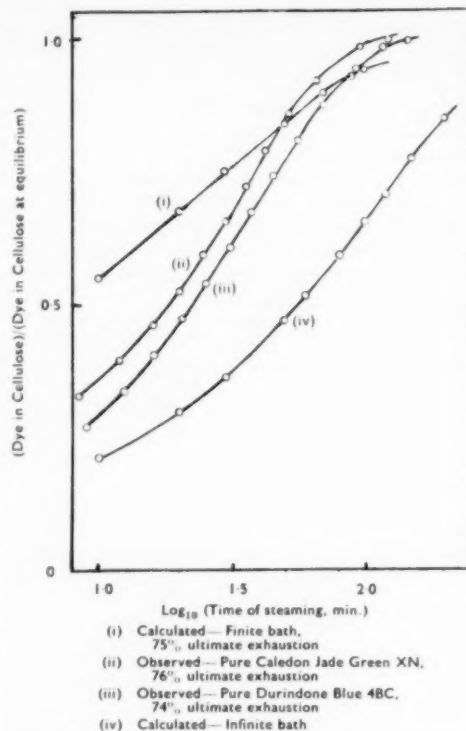


FIG. 4.—Observed and Calculated Dye Transfers during Steaming

the experimental curve agreed more closely with the curve for "infinite" than for "finite" bath conditions. The result was unexpected, and he has put forward an explanation, of which the details are not altogether clear, in which he suggests that the sum of the normal surface charge of the fibre and the charge due to adsorbed dye ions regulates the proportion of dye ions in the bath which are available for transfer to the fibre, so that their concentration remains constant in spite of large changes in the total dye concentration.

The same type of analysis has now been applied to some printing systems, by Pomfret²¹ for Chlorazol Sky Blue FF and the moderately substantive acid dye Coomassie Red PGP, each from starch to cellulose sheet (Fig. 3), and by L. B. Hallows²³ for the leuco forms of two vat dyes Caledon Jade Green XN and Durindone Blue 4BC, also from starch to cellulose, in the presence of potassium carbonate and sodium formaldehyde-sulphoxylate (Fig. 4). It will be seen that, in the printing transfer also, Chlorazol Sky Blue FF (final exhaustion ca. 70%) diffuses more nearly as though it were applied from an infinite bath, whereas for Coomassie Red PGP the comparison is indecisive, for at the low bath exhaustion reached (22.5%) there is little difference between the "infinite bath" and the "finite bath" curves. With the two vat dyes, the transfer behaviour also corresponds more closely to "infinite bath" conditions. If the original method of examination has a real power of discriminating between different dyeing mechanisms, this agreement, in spite of the many departures from the

experimental conditions of normal dyeing processes, is interesting and encouraging. It seems to show that the printing processes should ultimately be amenable to rigorous quantitative examination.

The establishment of infinite bath conditions in the thickener layer during steaming may come from a variety of different causes. The behaviour of the vat-dye systems, with their high accompanying concentrations of electrolyte, does not suggest that the transfer of dye from the "bath" can be regulated primarily by the surface charge on the cellulose. But infinite bath conditions may be more readily set up in printing than in dyeing. The high concentration of dye in the water-swollen thickener phase may cause saturated solutions of dye to be maintained there during most of the steaming period, and the effective concentration may be kept constant in this way. H. B. Hallows²⁴, examining cross-sections of the printing system during the transfer of Chlorazol Sky Blue FF, has found that there is a thin layer in the starch, immediately contiguous to the cellulose, which has been denuded of most of its dye, suggesting that this dye is passing into the cellulose quicker than replacements can diffuse in from the rest of the starch. If this is caused by a chemical attachment between dye and starch molecules, there exists an alternative mechanism for keeping the effective concentration of dye presented to the cellulose more nearly constant.

In Crank's exhaustion-time curves, and in those just illustrated, the slopes of the experimental curves are greater not only than the slopes calculated for the finite bath but also than those for infinite bath conditions. This may possibly be referred to the fact that a diffusion coefficient independent of concentration has been assumed, although Crank and Henry²⁵ have suggested that variation of diffusion coefficient should not affect the relation. Crank himself has shown that the diffusion coefficient does vary, and, for this reason among others, one of us was led to examine the results obtained during the printing transfer of Chlorazol Sky Blue FF from starch to cellulose with the object of finding how the concentration of dye in the cellulose affected the value of the diffusion coefficient.

CHANGE OF DIFFUSION COEFFICIENT WITH DYE CONCENTRATION

This investigation followed long and imperfectly successful attempts to bring the starch phase and the cellulose phase separately into a condition of steady moisture interchange with the steam before contact was established and dye transfer permitted. From these experiments, however, a technique was developed in which the water content of the printing system could be maintained constant during the whole period of dye transfer, instead of rising steadily, as Pomfret has shown, when the printing system is suspended directly in steam. Thus, while the experimental system preserved the form of the printing systems examined in earlier work, the constant water content made them more plausibly comparable with dyeing systems. One thing soon became clear: the higher

the water content of the system examined under these conditions, the more rapid the dye transfer and the greater the proportion of dye transferred at equilibrium (Fig. 5). Then at a constant water content, and with different initial dye concentrations in the starch, a family of adsorption-time

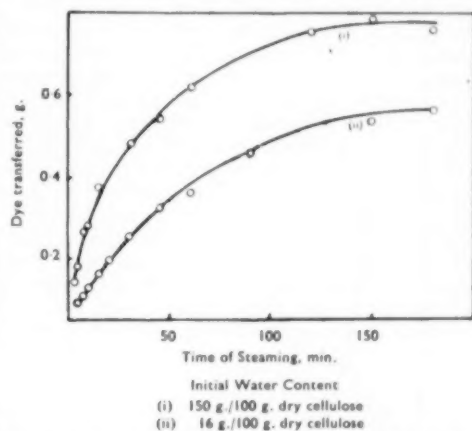


FIG. 5—Effect of Moisture Content of System on Transfer of Pure Chlorazol Sky Blue FF from Starch to Cellulose

curves was obtained. For each of these, a mean value for the apparent diffusion coefficient \bar{D} was calculated, according to the method of Crank and Park¹³, and then, for the whole series, the equation—

$$\bar{D} = \frac{1}{c_0} \int_0^{c_0} D \, dc$$

was differentiated to give the true diffusion coefficient D at different concentrations of dye in the cellulose, by a graphical method based on that of Crank and Henry²⁶. The results for pure

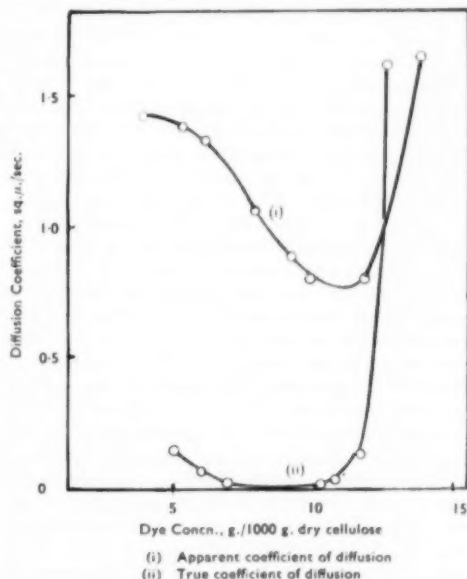


FIG. 6—Change of Diffusion Coefficient of Pure Chlorazol Sky Blue FF with Concentration in Cellulose, constant water content in system

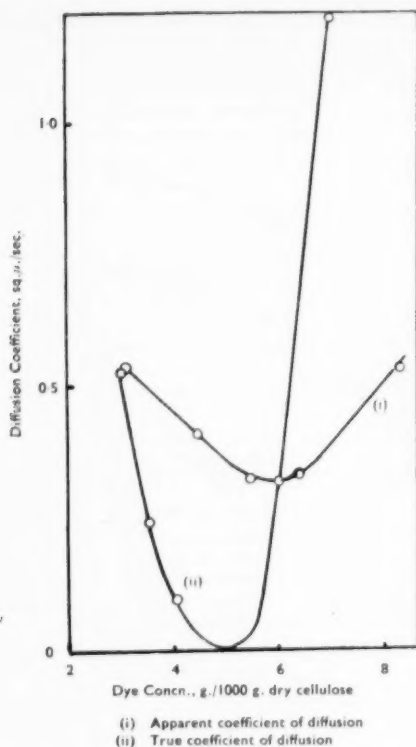


FIG. 7—Change of Diffusion Coefficient of Pure Chlorazol Sky Blue FF with Concentration in Cellulose¹⁶

Chlorazol Sky Blue FF are given in Fig. 6. The experimental data for the transfer of the same dye obtained by Munshi¹⁶ are treated in the same way to give the curves shown in Fig. 7. In the latter experiments, of course, no special precautions had been taken to keep the water content of the system constant. The two sets of calculations agree in showing a variation of D with c quite different from the linear relation found in the dyeing of direct cotton dyes. The diffusion coefficient in the printing experiments passes through zero. By this reasoning, therefore, there is a local concentration of dye in the cellulose at which diffusion stops. How this conclusion can be interpreted in terms of the behaviour of an actual printing system will require further consideration. Inspection of values for D calculated by Crank from experiments by Neale with the same dye at 95°C. shows that their range is 1.5×10^{-9} sq.cm./min. over a concentration range of 0–20 g. dye per litre. In the present printing experiments, they range from a very small value to 16×10^{-9} sq.cm./min. for an estimated change in concentration in the water of the cellulose from 1 to 1.3 g. dye per litre. The temperature is very close to 100°C. Diffusion of dye thus tends to be faster in the printing experiments. The significance of the minimum requires a longer discussion than is appropriate here. It is obvious that the cellulose is in different physical conditions in dyeing and in printing systems. In measurements of the density of cellulose²⁷ dyed

with different concentrations of Chlorazol Sky Blue FF, there is evidence first of a volume contraction and then of a volume expansion as the concentration of dye in the fibre-substance is increased. The point of inflexion occurs at concentrations not very different from those at which the diffusion coefficient reaches the minimum value, and this suggests that certain concentrations of dye can draw the fibre-structure together. This can, perhaps, modify a diffusion process in which, in the lower range of concentrations, an increasing proportion of dye passing through the pores is adsorbed on the walls as the total concentration is increased, up to the point at which the minimum value for D is reached. Thereafter an increase in concentration will provide more and more dye in excess of that which can be taken up during passage, and the coefficient then increases towards the limiting value for free diffusion. If the adsorbed dye can assist in swelling the cellulose, this effect would be enhanced, and the very rapid rise of the diffusion coefficient with concentration at this stage could be more readily understood.

ADSORPTION ISOTHERMS

Adsorption isotherms express the relation between the amount of dye taken up by the fibre-substance and that remaining in the external medium when some well marked stage in the transfer process, generally equilibrium, has been reached. The study of adsorption isotherms in dyeing systems has yielded a good deal of information, giving in some cases an indication of the adsorption mechanism, and in others, additionally, a more or less quantitative measure of the strength of the chemical bonds which bind fibre molecules and dye molecules together. In the printing experiments, our knowledge of the systems does not yet seem sufficiently detailed to allow any very numerous calculations of the strength of chemical attachment. In dyeing, the resultant partition of dye comes from the relative strengths of attachment of dye molecules to water and to fibre-substance respectively. Quite often the strength of attachment to water is relatively so uniform, consistent, and uncomplicated that it can be disregarded. In printing, the exterior medium, a water-swollen layer of a high-molecular colloidal structure, offers many more problems. We should study the adsorption of dye from water by starch to give us half the necessary data, and the difficulties of this study, while not obviously insuperable, are certainly very great. Therefore, in this review, only one or two examples of characteristic printing isotherms can be discussed.

Direct Cotton Dyes and Cellulose

In the paper by Munshi and Turner¹⁶ the isotherm for the transfer of Chlorazol Sky Blue FF from starch to cellulose was found to be irregular. A re-examination of their results for 600 PT Cellophane sheet, and a comparison with transfers to 300 PT sheet, with the water content of the system maintained constant, suggests that the irregularities are probably due to experimental error, and that the isotherms are almost straight

lines for much of their length, although they do not pass accurately through the origin if the straight part is produced, and the slope tends to diminish as the higher dye contents of the system are reached. It cannot be said that there are yet sufficient data, in respect of either variety of transfer conditions or variety of dyes examined, to allow detailed conclusions to be drawn.

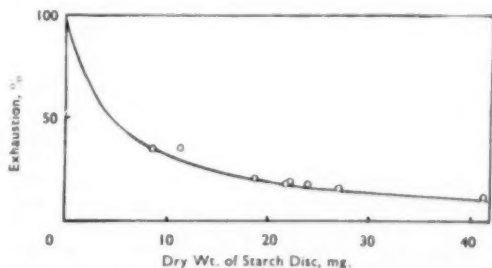
Acid Dyes and Cellulose

The work of Patel and Turner¹⁸ revealed very unusual transfer characteristics for dyes which occur in Meitner's classification²⁶ as having low or moderate aggregating powers in aqueous solution. The rate-of-transfer curves for these dyes were shown to pass through more or less well marked maxima at times varying from 10 to 60 min. from the beginning of steaming, and to approach, but not to reach, equilibrium after prolonged steaming. Further, the exhaustion was shown to increase with increase in the dye concentration in the starch phase. Since equilibria have not been attained, isotherms have been constructed by Patel and Turner¹⁸ showing the distribution of Coomassie Brilliant Blue FF (ICI) between starch and cellulose at the time corresponding to maximum transfer, which is approximately 1 hr. for all concentrations. The result is a straight line which cuts the dye-in-starch axis at some distance from the origin, and this has been thought to indicate the presence of a small proportion of basic groups in the starch or some other influence which renders a small constant weight of dye less readily transferable than the rest. Pomfret²¹ has repeated the experiment with a more readily soluble dye, Naphthalene Red EA. In this dye, a maximum is established very early in the steaming, so that the dye partition after 3 hr., when the change in partition is slow, was used instead of the maximum value. He, too, with a dye which is different from Coomassie Brilliant Blue FF in many other respects, found the straight-line relation, the produced curve also cutting the dye-in-starch axis at a positive value.

In an early attempt to explain the formation of the maximum, it was suggested that it might always occur with a very highly dispersed dye having a low affinity for cellulose. The sole controlling factor in the diffusion process, in the ideal case, would be the concentration gradients in the system. At the beginning, with all the dye deliberately in the thickener phase, and with water supplied from the steam, dye would go into the empty cellulose phase. Later, with the starch taking up more water than the cellulose, the concentration of dye in the former phase would be diminished, and the concentration gradient reversed in direction. Pomfret has spent much time in attempts to verify this idea directly by determining the distribution of the total water content of the system between the two phases during the course of steaming, so that it could be compared with the corresponding dye distribution. Unfortunately, no method has yet been found of making this measurement when the phases are in contact.

Another method of approach was tried. For the same steaming time, and with the same weight of

dye in the system for unit area of contact between starch and cellulose, it is possible to change the proportions of water in the respective phases by altering their relative weights, in this case by altering the relative thickness. It is easier to alter the thickness of the starch film than that of the cellulose film. The results will be only approximate, because it was found, in measuring the uptake of water from steam by a starch film alone, that the specific increase in weight depended upon the actual dimensions of the sample, area as well as thickness, so that it appears that the entry of water into the edge has an influence that cannot be neglected. Nevertheless, calculating from the change in thickness of the phases, and allowing for the small proportion of non-diffusible dye in the starch, mentioned above, the distribution of the dye Naphthalene Red EA was predicted, and is shown in Fig. 8 as a continuous curve. The directly



Curve — Transfer calculated from assumed water distribution in system
Points O Experimental determinations

Fig. 8.—Transfer of Pure Naphthalene Red EA to Cellulose from Starch Films of Different Thicknesses during Steaming for 3 hr.

determined partition values for the dye are shown by the separate points. The agreement suggests that the original hypothesis, that dye distribution is determined by water distribution, is fundamentally correct.

Some of the difficulties in applying this hypothesis to a number of dyes have been expressed already. It should mean that all "indifferent" dyes in starch-cellulose should have their maximum partition at times which are not very different and are primarily determined by the water-absorption properties of the two phases. But this is not true. Naphthalene Red EA and Coomassie Brilliant Blue FF have maxima at very different times. Dastur²⁰ has recently studied the transfer of these two dyes when they are present together in a single starch-cellulose system. Fig. 9 shows that they keep their identity of transfer behaviour in the presence of each other, so that changes in the two media of the system which might be considered to affect the one dye are ignored by the other, and *vice versa*.

It is interesting to find another departure from the behaviour observed with other classes of dye during dyeing. From Fig. 9 it is seen that, without any substantial alteration in the shape of the exhaustion-time curve of either dye, the actual exhaustion values of the one are increased by the presence of the other. With direct cotton dyes, we have found the same effect as that found by Neale for dyeing, where the presence of one dye diminishes

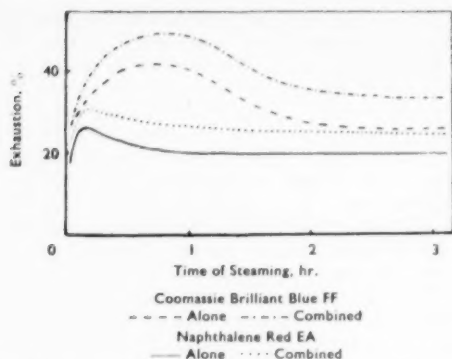


FIG. 9—Transfer of Coomassie Brilliant Blue FF and Naphthalene Red EA from Starch to Cellulose on Steaming, alone and in combination

the exhaustion of another when the two are introduced together into the same starch film.

Vat Dyes and Cellulose

In carrying out transfer experiments with vat dyes between starch and cellulose by the procedure adopted for other dyes, L. B. Hallows²³ found that special working conditions were necessary. It was not possible to avoid the simultaneous presence of relatively large proportions of reducing agent and alkali in the starch film, along with the dye. It was possible to reduce the consumption of the Formosul by steaming in oxygen-free vapour provided by boiling water containing reducing agent and alkali. The presence of potassium carbonate and Formosul in the film, however, caused it to take up so much water from the steam that the combined starch-cellulose samples had to be steamed with special precautions to avoid running of the starch. However, this behaviour

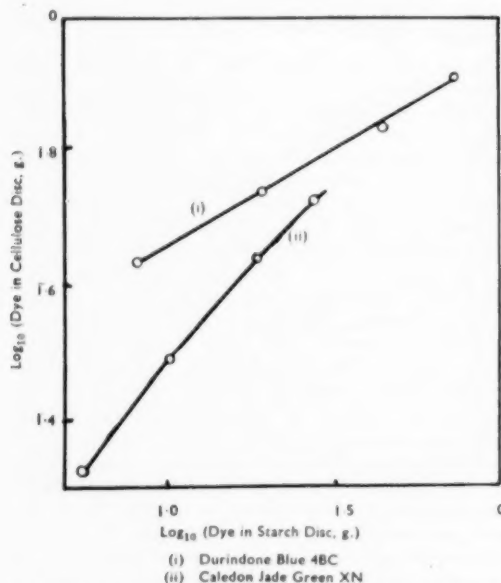


FIG. 10—Isotherms for Partition of Caledon Jade Green XN and of Durindone Blue 4BC between Starch and Cellulose on Steaming to Equilibrium

was not without its advantages, for it brought about a very large water uptake in the system during the early stages of steaming, after which the proportional change in water content was not very great. When the logarithm of the weight of dye present in the unit disc of starch at equilibrium is plotted against the logarithm of that present in the corresponding unit disc of cellulose, a straight line results for Durindone Blue 4BC and almost a straight line for Caledon Jade Green XN (Fig. 10). This indicates that the equilibrium partition is best expressed by the Freundlich isotherm, which has been shown to define the equilibrium dyeing conditions for a number of direct and of anthraquinonoid vat dyes on cellulose²⁹.

Disperse Dyes and Cellulose Acetate

In a recent paper, Daruwalla and Turner³⁰ have given an account of experiments to determine the partition of typical disperse dyes between starch and cellulose acetate during steaming. Here the behaviour of the dye is very simple. At equilibrium it divides itself in a constant ratio between the starch and the cellulose acetate, independently of the amount of dye present, until with increasing proportion of dye the cellulose acetate can take no more. The saturation point is very sharply defined for such a system. An isotherm is shown in Fig. 11. In another paper,

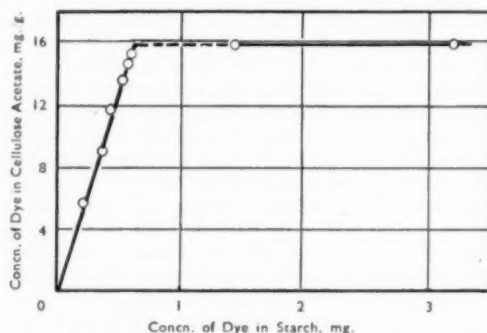


FIG. 11—Isotherm for Distribution of Pure Durandol Red 2B between Starch and Cellulose Acetate during Steaming

the same workers³¹ have observed similar behaviour in the transfer of the same disperse dyes from starch to nylon. The behaviour is analogous to the partition of the dye between water and a non-miscible liquid, such as amyl acetate, when all three are shaken together and allowed to settle, and the process by which dyeing occurs may be called "solid solution". Vickerstaff and Waters³² investigated the dyeing of cellulose acetate with suspensions of disperse dyes, paying special attention to the possibility of "solid solution". They found that the straightforward process was complicated by other effects, which made the evidence for "solid solution" processes a little uncertain. It is rather remarkable that this evidence should be furnished so unambiguously in a printing system, where, it might be thought the risks of its being obscured by other effects would be even greater than in dyeing.

The foregoing examples, which have only been sketched in outline, have been brought together so that it may be seen that there is a real possibility of applying the quantitative methods developed for the study of dyeing processes to analogous printing processes. Often this application will bring out the essential unity of dyeing and printing methods, but, as shown in some of the examples, the behaviour of printing systems may be quite unusual and unexpected.

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(MS. received 24th July 1953)

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Discussion

Mr. C. P. ATKINSON: With reference to the rate of dye transfer in both dyeing and printing operations what consideration has been given to the effects of preparatory processing treatments in that there is a direct relationship between dye distribution, etc., and fibre surface energy. Again, as regards yield and colourfastness, etc., it is possible that a pre-determined set of preparatory processing conditions will give optimum results with any particular dye formulation. Whilst appreciating that the question of suitable preparatory processes, including mercerising and bleaching treatments are generally more variable in character, influenced by local conditions and customers' particular requirements, etc., than those referred to in the excellent and comprehensive survey by the authors, I suggest that the matter is of such importance as to warrant consideration being given by the committee concerned, so as to determine if it is possible for the subject of "preparing of all types of textile materials" being the basis of a future symposium.

Mr. H. A. TURNER: While I agree that the preparation of the cloth to be printed may have a great influence upon dye transfer and fixation; and while I think that investigations like those suggested by Mr. Atkinson may yield very useful technical information, I cannot see how any of our results can be interpreted so as to make a useful contribution to the problem. With us the fibre substance is mostly represented by a film of regenerated cellulose from which, presumably, all the natural impurities have been removed and which must already be much closer to fully mercerised cotton than a normal bleached cotton would be.

Mr. A. S. FERN: The relative affinities for cellulose of Durindone Blue 4BC and Caledon Jade Green XN shown in Fig. 10 do not correspond to general dyeing experience or to the

printing behaviour described in Table II of the previous paper (Michie and Thornton). Is the lecturer sure that equilibrium was reached in these experiments (particularly with Caledon Jade Green XN, which possesses a comparatively large molecule)? If this is believed to be the case, what explanation is given for the apparently greater absorption of Caledon Jade Green XN by starch?

Mr. TURNER: Unfortunately the range of vat dyes which has been examined by our method is small, and little more than a guess can be given. The equilibrium values for dye partition upon which the curves are based correspond to steaming times of 180 min., and the exhaustion has remained constant for at least 70 min. Soon after this time, the equilibrium of Durindone Blue 4BC is disturbed for some unexplained reason and the exhaustion rises sharply again. It may be associated with incipient oxidation of the leuco-compound. The maximum steaming times were much shorter in the experiments of Thornton and Michie. In the film technique the ratio of starch to fibre substance (ca. 2:1 to 3:1) is probably much higher than it will be in a normal print, and this may account for the low exhaustion to cellulose. It is stated in the paper that the relative affinities of direct dyes for starch and for cellulose may vary greatly from dye to dye. The same may be true for leuco-vat dyes, and the differences may be seen more clearly when the proportion of starch is high.

Dr. T. VICKERSTAFF: I cannot see that the maxima in the steaming curves for acid dyes shown in Fig. 9 present any serious difficulty in interpretation. If the dye was distributed initially throughout the whole system in accordance with the distribution of water, then on steaming, the moisture content of the starch paste would steadily increase and the dye concentration in the cellulose would steadily fall. In effect however, the dye is

initially present in the dye paste and must first migrate into the cellulose, consequently, there are two opposing processes in action and the concentration of the dye in the cellulose will rise to a maximum and then fall. The position of the maximum on the time scale will be determined by the rate of diffusion of the dye and will occur earlier with dyes that diffuse rapidly. This is clearly displayed in Fig. 9. The lack of sensitivity of Naphthalene Red EA to moisture uptake as compared with Coomassie Brilliant Blue FF may well be due to the greater affinity of the latter dye.

MR. TURNER: If I understand Dr. Vickerstaff rightly, he can see why the same change in moisture distribution between starch and cellulose is able to account for the early reversal in dye transfer with Naphthalene Red EA and for the much later continued reverse migration of Coomassie Brilliant Blue FF (Fig. 9). It is just this conclusion which is causing us difficulty. From Fig. 2 it is seen that the relatively greater water uptake of starch is only substantial during the first 40 min. or so of steaming time. This seems to be confirmed by the transfer results with the soluble, non-aggregating rapidly diffusing dye Red EA. As Dr. Vickerstaff says, the first migration of dye will be from the high-concentration region in the starch to the zero concentration in the cellulose. As the latter phase fills up with dye, the concentration difference diminishes ultimately to zero, with a corresponding diminution in rate of dye transfer to cellulose. This is without any accompanying change in the water distribution between starch and cellulose. But the starch is filling up more rapidly with water, reducing the initial concentration difference more rapidly than forward diffusion alone could do, slowing this diffusion down and, at length, reversing it. The incentive towards reverse diffusion will now continue for as long as the gain of water by starch is greater than the gain by cellulose, say 40 min. Red EA, being able, by quick diffusion, to adjust itself rapidly to these changes, has passed through the point of maximum exhaustion to cellulose in about 10 min. and, after about one hour, a net reverse migration has almost ceased. Coomassie Brilliant Blue FF diffuses more slowly into the cellulose and will, therefore, it is true, diminish the concentration difference (causing this diffusion) less rapidly. Preferential acquisition of water by starch is, however, continuing simultaneously and forward diffusion of the dye will be brought to a

standstill somewhat later than for Red EA. This preferential water uptake does not, however, go on indefinitely so that the incentive to the reverse migration has disappeared before the exhaustion reaches its maximum value. It is difficult to see, therefore, what causes the continued decline of the exhaustion up to periods of two hours from the beginning of steaming. It cannot be the same adjustment in the distribution of water in the system which has caused the transfer peculiarities of Red EA. If it is some later disturbance in the starch-cellulose system, it would be expected to cause corresponding changes in the Red EA transfer when the two dyes are transferred together. These are not observed. We have found that solutions of Coomassie Brilliant Blue FF, at concentrations well below those which are calculated from the dye and water content of the starch phase in steam, are very viscous and it is obvious that molecular aggregation is far advanced. An aggregation-disaggregation mechanism, probably operating in each phase, may therefore have to be examined as a partial cause of the peculiar migration behaviour of Brilliant Blue FF.

MR. J. W. RYCHOF*: Perhaps Dr. Vickerstaff in his explanation of Fig. 9 may oversimplify the whole. There may be at least four factors influencing the rate of dye transfer, viz.—

(a) rate of diffusion from the water-containing thickener (starch) phase to the water-containing fibre-phase.

(b) water-migration, due to inequalities in water-uptake of both phases, which is of particular interest if the dye is water-soluble.

(c) rate of adsorption of dye at the fibre.

(d) rate of adsorption of dye at the thickener molecules.

Whereas the equilibrium state may be influenced by—

(a) coefficient of adsorption of dye at the fibre.

(b) coefficient of adsorption of dye at the thickener molecules.

(c) coefficient of partition of unadsorbed dye in both water-containing phases (although this coefficient in many cases will be very near to 1).

The explanation of the minimum in the curves of Fig. 6 and 7. I do not see how an increase in concentration can cause a decrease in adsorption at the walls of the pores.

* Communicated

FRIDAY AFTERNOON, 25th SEPTEMBER 1953

Chairman — G. S. J. WHITE, Esq.

Developments in the Application of Azoic Dyes in Printing

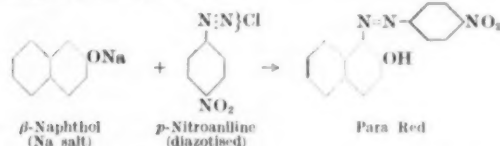
B. JOMAIN

A brief review is made of the development of azoic dyes for printing, from the original application on β -naphthol prepares, via the Rapid Fast and Rapidogen ranges, to the recently introduced neutral-steaming dyes. The application of these new dyes in multicolour styles is discussed in some detail.

To-day the insoluble, azoic dyes offer an important range of bright shades, possessing excellent general fastness and characterised by ease of application.

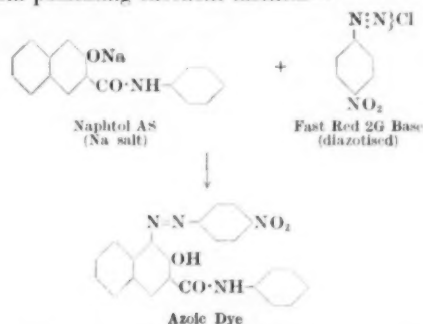
This position is the outcome of work started little more than half a century ago by such workers as Koechlin and Ulrich in Germany and Thomas Holliday in England, who established the principle of the formation of azoic dyes ("ice colours") directly on the fibre by impregnation with a phenolic derivative and subsequent treatment with a diazo solution.

For many years β -naphthol was used as the coupling component—



but the naphthoxide had poor stability and the all-round fastness was not good.

The use of β -naphthol was superseded on the introduction of the Naphtol AS series, which are the arylides of 3:2-hydroxynaphthoic acid, and which offered a much wider range of colours, many of them possessing excellent fastness—

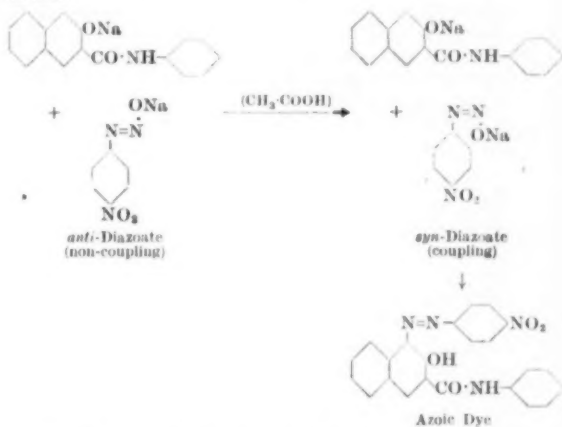


The stability and the reliability of the naphthoxides were much improved.

However, impregnation in the Naphtol, requiring special and often costly equipment for padding and drying (hot flue) led research workers to the production of compositions in which the diazo component was rendered stable and unreactive, so that it could be associated with a Naphtol AS derivative within the print paste, subsequently to be regenerated and form the azoic dye on the fibre.

The Rapid Fast series, introduced by the Chemische Fabrik Griesheim-Elektron in 1915,

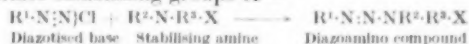
were obtained by the association of Naphtols with the *anti*-diazates of various amines, and were developed on the fibre either by neutral steaming—allowing their use alongside vat dyes—followed by an acid bath, by acid steaming, or even by hanging in air.



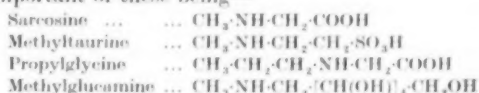
Rapid Fast Red 2G = Mixture of Naphtol AS (Na salt) and Na *p*-nitrobenzene-*anti*-diazate (Fast Red 2G)

The stability of the print paste was limited to several days, but this difficulty was overcome some years later with the introduction of the Rapidogen dyes by the IG. Farbenindustrie AG. The success of this range was immediate, and research workers all over the world began to investigate this new field.

The Rapidogens are mixtures of diazoamino derivatives of "fast bases" and the usual coupling components used in the "ice colour" technique. The diazoamino compounds (triazens) are obtained by the action of a diazonium salt on a primary or secondary stabilising amine containing the appropriate solubilising groups X—



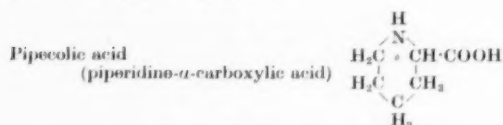
Hundreds of stabilising amines are cited in patents or have been investigated, but only a few have been manufactured industrially, the most important of these being—



This last compound was first used by the IG, but is now replaced by—



(R = CH₃, C₂H₅, or C₄H₉) or—



These dyes generally require for their development an acid treatment which regenerates the diazo component. Several methods can be envisaged for their fixation, but the only one of importance is steaming in the vapour of acetic or formic acid. This process leads to rapid corrosion of the metal parts of the steamer, against which there is no effective protection. Furthermore, the Rapidogens when applied by this method cannot be printed alongside vat dyes, a double steaming, first neutral and then acid, giving very irregular results.

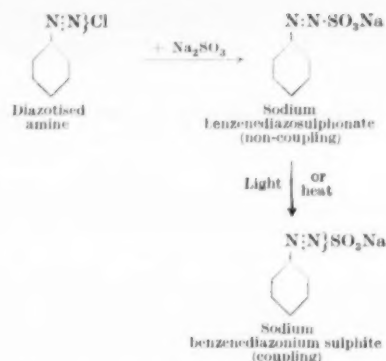
Experiments have therefore been undertaken to eliminate acid steaming and thus permit the association of Rapidogens with vat dyes. Generally this necessitates the incorporation in the print paste of agents which produce the acids necessary for the hydrolysis of the Rapidogen during the course of a short neutral steaming. Amongst those which have been investigated are the esters and the salts of organic and mineral acids, e.g. potassium bromoacetate, sodium chloroacetate and trichloroacetate, potassium fluorosulphonate, and sodium acetoxyethanesulphonate.

Such methods have each been abandoned after a short trial period because of irregularities in development, inferior stability of the print paste, and the need for critical concentrations of caustic soda.

An entirely different process is the Rapidogen Developer N technique, in which the caustic alkali is replaced by a volatile amine (diethylamino-ethanol) and development is effected simply by neutral steaming, during which the amine is removed and the acidity of the hydroxy group of the coupling component is generally sufficient to split the diazoamino derivative. Results obtained by this process are often irregular; and, furthermore, it does not allow the use of Rapidogens alongside oxidation blacks because of the alkaline vapours evolved. Finally, the cost of the volatile amine has been so high as to limit its use.

In the Rapidazol (IG) series, the diazo component has been transformed into the diazo-sulphonate, which can be developed only in neutral steam. The restricted range available has, however, prevented them from achieving the success expected.

A similar principle is used for the Photo Rapids of St. Denis, which are developed by exposure to sunlight, mercury-vapour lamps, or electric arcs—

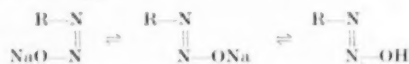


A different technique was employed for the Cibagenes (Ciba), in which soluble derivatives are used which regenerate the amine, and this is diazotised in the presence of sodium nitrite in acid media to give the diazo component, which in turn couples with the naphthoxide, producing the azoic dye. These dyes are developed on the fibre by padding with a thickened solution of formaldehyde and hydrochloric acid.

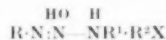
The Neocotone (Ciba) dyes are azo dyes rendered soluble by the introduction of solubilising groups and regenerated in the fibre by a final treatment with barium hydroxide and sodium chloride. As they require only neutral steaming before this treatment, they lend themselves to association with vat dyes.

Throughout this brief survey it can be seen that the tendency has been towards the production of a range of azoic dyes, of easy application, developed simply by neutral steaming, which will permit their association with other classes of dye, particularly vat dyes.

Between the hydrolysis in alkaline media, which has been exploited for the neutral steaming of the Rapid Fast types—

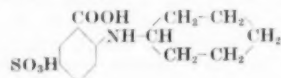


and the hydrolysis in acid steam of the Rapidogens—



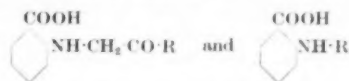
appropriate stabilising amines have been sought which allow hydrolysis of diazoamino derivatives even under alkaline conditions.

Kuhlmann¹ and the IG² describe the use of diazoamino derivatives containing a substituted or unsubstituted sulphonamoyl group and one or more carboxyl groups. Kuhlmann³ suggest also the use of *N*-cyclohexyl-5-sulphoanthranilic acid—



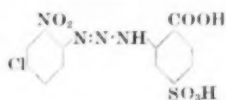
mentioning the extreme rapidity of hydrolysis in the cold of compounds obtained with this stabiliser.

The Compagnie Française de Matières Colorantes have carried out investigations on the *N*-substituted anthranilic acids of formulae—



(the benzene nucleus may be substituted by one or several halogen atoms, or by one or several alkyl or alkoxy groups; R = alkyl, cycloalkyl, or substituted cycloalkyl).

As is known, no universal stabiliser has yet been found, each diazoamino derivative possessing a different rate of hydrolysis according to the nature and number of the substituting groups in the nuclei of the diazotised base and of the stabilising amine. For example, the compound obtained from 4-chloro-2-nitroaniline and 4-sulphoanthranilic acid—



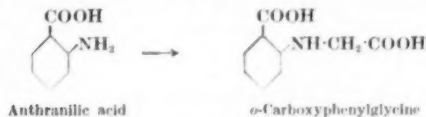
does not hydrolyse under practical conditions in acetic acid vapour. Compounds from the same 4-sulphoanthranilic acid and 2-methyl-4-nitroaniline or 2:5-dichloroaniline hydrolyse incompletely and the yield is bad. On the other hand, with the same diazo components and an *N*-substituted sulphoanthranilic acid the rate of hydrolysis and the yield are considerably increased.

The ideal solution would be to have for each diazotisable base the appropriate stabiliser, but most manufacturers have restricted themselves to two or three suitable amines.

For diazo components of strongly basic character, such as 4-benzamido-2:5-dimethoxyaniline and *p*-amino-*p'*-methoxydiphenylamine, the amines generally used are sarcosine, methyltaurine, and methylglucamine. For weak bases (nitroanilines, dichloroanilines, and trifluoromethyl derivatives) *N*-ethyl-5-sulphoanthranilic acid is generally used.

Thus, with the Neutrogenes, a careful choice had to be made from the many stabilising agents available, in order to produce for the user a range of dyes of good stability and easy application, and giving completely reliable development in neutral steam.

Fortunately, there is quite a wide choice of suitable stabilising agents—e.g. *o*-carboxyphenylglycine, its 3-, 4-, and 5-chloro, dichloro, and



methoxy derivatives, and esters and amides of these acids; *N*-alkoxyanthranilic acids and their derivatives substituted in the benzene ring, and *N*-alkylanthranilic acids and their substitution products; *N*-*o*-carboxyphenyl- β -aminopropionic acid and its derivatives; *N*- β -hydroxy- γ -sulphopropylanthranilic acid; and others are still being developed in our laboratories.

The field of application of the Neutrogenes is very wide, as they may be used for printing cotton, viscose rayon, and, with suitable modification to the recipe, silk.

The range to date consists of eleven dyes, many of which can be mixed to give a wide variety of shades, and it is expected that this will be extended in due course. The Neutrogenes are finding widespread application both as a means of eliminating acid steaming and also for association with other classes of dyes, many of which are deficient in certain colours. For example, vat reds and scarlets of the indigoid type may be replaced with advantage, the Neutrogenes giving faster and brighter results at lower costs. Furthermore, oxidation difficulties are eliminated and there is no possibility of tendering.

PREPARATION OF THE PRINT PASTE

This is a simple procedure, the dye being pasted with the requisite amount of caustic soda and dispersing or dissolving agent (thiodiglycol) and then dissolved in tepid water. Urea or alcohol can be used, but the colour yield and brightness are slightly inferior.

The Neutrogenes are practically insensitive to the concentration of caustic soda. By increasing it, coloured resists under aniline black can be produced with Neutrogene Light Yellow 4J and Neutrogene Yellow J Extra. On the other hand, by reducing it, conditions suitable for the printing of silk are obtained. Indeed, in this latter connection, laboratory trials indicate that the caustic soda may be replaced by potassium carbonate or even trisodium phosphate.

The caustic soda concentration has an important influence on the keeping qualities of the print paste. The recommended recipes give a stability of the order of two to three weeks; but if, for example, the caustic soda concentration is doubled, the stability is greatly increased, although at the same time the brilliance of the print may be slightly inferior.

The print pastes should be stored in a cool place protected from light and from acid vapours.

The recommended thickening is starch-tragacanth, although this may be replaced either partly or completely by certain carboxymethyl celluloses (except when working with neutral chrome). Thickenings of a reducing nature should be avoided.

Because of the sensitivity of the Neutrogenes to reducing agents, it is essential (except with Neutrogene Light Yellow 4J and Neutrogene Yellow J Extra) to incorporate in the print paste a protective agent such as sodium chlorate, sodium *m*-nitrobenzenesulphonate (Resist Salt O), or Neutrogene Salt ON Paste. Sodium chlorate, offering only limited protection in alkaline media, should not be used in concentrations exceeding 1%, as a larger amount does not improve the anti-reducing effect and can lead, in the most unfavourable cases, to the formation of oxycellulose.

Resist Salt O or Neutrogene Salt ON Paste can be used in concentrations of approx. 2% when printing alongside direct, chrome, soluble vat, Solanile Black, and pigment dyes. When printing alongside vat dyes, particularly when these are in large areas, the concentration of protective agent should be

increased to 5–7%. Better results are obtained with Neutrogene Salt ON Paste, which is more soluble in alkaline media than Resist Salt O and has a greater protective effect even when used at lower concentrations.

Finally, when printing Neutrogene Light Brown B, neutral chromate is used as the protective agent.

APPLICATION IN MACHINE AND SCREEN PRINTING

When Neutrogenes are screen-printed alongside other dyes, there are no special precautions to be taken. In general, printers apply the Neutrogene first, but this is immaterial. For full-on outline blacks, sulphur blacks of the Sulfanol Fast Black CLA type are recommended, these being printed first down. Solanile Black can also be used by printing first, leaving on the table overnight to develop the black, and then printing the Neutrogene.

In machine printing alongside other dyes, any order of printing may be used, except with vat dyes, where it is recommended that the Neutrogene should be printed last. The print paste will withstand the inevitable carry-over of a small quantity of vat paste, which may be minimised by the use of a starch roller. On the other hand, the Neutrogenes are sensitive to crushing by the rollers printing the vat dyes.

For the same reason, when printing sulphur blacks as outlines, the Neutrogenes should be printed last.

The Neutrogenes are characterised by excellent working properties in the machine, and unlike their predecessors have no tendency to give doctor streaks, scumming, facing, etc. As a sighting colour we recommend the use of 0.1–0.3% Detector Red B.

In large blotches the Neutrogenes level perfectly. This is particularly interesting on rayon staple, a fabric which causes difficulty with certain azoic printing dyes. In screen printing, for example, they print so evenly that it is difficult to recognise the repeat of the design.

DEVELOPMENT

The printed pieces do not require any special precautions during storing before steaming. Development may begin at the selvages, for example, but final steaming will cause these irregularities to disappear. A slightly acid atmosphere can only accentuate this premature development, and is without detrimental effect on the final yield.

A neutral steaming of 3–7 min. in moist steam completes the development of the colours, giving full yield and brilliance. Excessive pressure or overheating may dull the colours slightly, this being accentuated with prolonged steaming times such as are encountered in the fixation of direct or chrome dyes. With chrome dyes, however, the organic acids used in the print paste, which volatilise in the steam, protect the Neutrogenes from this effect. On the other hand, with direct dyes prolonged steaming in a neutral atmosphere dulls the colours, particularly the reds and the scarlets, and this cannot afterwards be corrected, although a treatment with hydrosulphite, sodium carbonate, and a detergent may effect an improvement.

Most of the Neutrogenes steamed in the presence of aniline vapour may be dulled, and the reds and scarlets are browned more or less considerably. Only Neutrogene Light Yellow 4J and Neutrogene Yellow J Extra are unaffected by this danger in close proximity. The use of Kollamine in the Aniline Black increases the dulling effect still further. Care should therefore be taken to see that the steamer is free from aniline fumes before the prints are entered.

These dyes can, of course, be fixed by acid steam, although development is so rapid that a large amount of the dye is loosely fixed on the surface of the fibre. Hanging in warm moist air for 24 hr. or passage through a warm organic acid bath also fixes the Neutrogenes, although in these cases the yield is inferior.

Neutrogenes in combination with Indigosols, printed by the sodium nitrite process, will withstand the Indigosol wet developing process if they have previously been developed by hanging or steaming.

FINISHING

The printed goods must be rinsed in cold water and then soaped. With large blotches the soaping should start cold and the temperature should be raised slowly to 80–90°C. It is interesting to note that Neutrogenes developed by neutral steaming have little tendency to bleed during soaping, and this feature, together with their clean printing properties, ensures good whites. This is considered to be due to the fact that with neutral steaming the coupling component (naphthol) remains in the form of the sodium salt during the whole of the steaming process, whereas with acid steaming there is partial precipitation of the naphthol on the surface of the fibre.

FASTNESS

Most of the Neutrogenes have a light fastness which, in full shades, may be classified as good, or sometimes even excellent; for example, that of Neutrogene Light Yellow 4J is 7–8. This makes them suitable for furnishings, particularly as there is no possibility of tendering. For the production of pale pinks, which has hitherto been restricted because of the poor light fastness of Neutrogene Scarlet R when used in this depth, the two new dyes—Neutrogene Light Red STR and Neutrogene Red 2J—can now be used, as in very pale shades their fastness to light is 4–5. These have proved to be valuable for the printing of small motifs alongside vat dyes for wineryettes, underwear, etc., where in certain cases the indigoid vats have been known to cause difficulties when working with Dewey and Almey type blankets and washers.

Finally, the fastness to rubbing is excellent.

MIXTURES

Theoretically only those dyes which have a common coupling component may be mixed, but in practice we have observed that only combinations having hues which are widely separated (such as yellow and blue) show any risk of uneven development due to cross-coupling.

A mixture of 90% Neutrogene Red R and 10% Neutrogene Light Violet R, for example, gives an intense bright bordeaux, fast to light. Scarlet and reds are miscible in all proportions, and a shading of Neutrogene Scarlet R with Neutrogene Light Yellow 4J leads to very bright oranges, fast to light, and consistent in development.

Corresponding mixtures to the well known Rapidogen Yellow-Indigosol Green are possible, but in this case the nitrite method is used for the Indigosol. Development is by neutral steam, followed by passage through a sulphuric acid bath.

RESISTS UNDER OXIDATION BLACKS

Although for coloured resists under aniline black the Rapidogen dyes retain a certain superiority, with the exception of the yellows, the Neutrogenes

are quite suitable for this style when Solanile Black is used.

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COMPAGNIE FRANÇAISE DE MATIÈRES COLORANTES
SERVICE APPLICATION
BOÎTE POSTALE CREIL
(OISE)
FRANCE

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Discussion

Mr. F. J. E. BANNING: Has the lecturer any experience of printing these dyes on wool? I know a printer who has used Rouge Neutrogène J for the printing of woollen flags without tendering the wool seriously.

Monsieur B. JOMAIN: Printing trials on wool with Neutrogene dyes have been made by several organisations and our own laboratories. In general the results obtained are not perfect the shades being somewhat irregular and the handle modified. The harsher handle is due to attack of the wool by alkaline reagents in the print paste. We advise working in this case with reduced quantities of caustic soda, e.g. 0.5% or to replace it entirely with trisodium phosphate. The oxidising agents included in the print paste protect the Neutrogene dyestuff sufficiently against the reducing action of the wool fibre itself.

Mr. F. CROMPTON: Do the Neutrogene colours need to be cooled when piled on a truck prior to steaming or can they be steamed hot off the drying cans?

M. JOMAIN: Industrial trials made in England have shown us that pieces printed with Neutrogene dyestuffs may be steamed immediately after drying on the tins behind the printing machine, that is to say without the pieces having been cooled. The results obtained have been exactly the same as on pieces which have stood for several hours before steaming. The fastnesses to rubbing and washing as well as the yield being practically unaltered.

Mr. L. DRIESSEN: Can Neutrogene, as a resist under aniline black be applied in the two ways, viz. (1) printing the resist on white cloth and pad afterwards and (2) print on prepadded cloth?

M. JOMAIN: Neutrogenes have been tried in our laboratories and on the industrial scale as coloured resists under aniline black. When resists are printed on material previously padded in aniline black, this corresponds to the usual method of working on the Continent, only Neutrogene Light Yellow 4J and Neutrogene Yellow J Extra gave us good results. Trials are under way with a view to finding a means of employing the other Neutrogene colours which, by the usual methods, are seriously flattened by the aniline fumes during the course of

the steaming. If the coloured resists in Neutrogenes are printed before padding in aniline black, i.e. following the usual method of working in England, it is possible to use not only the Neutrogene yellows, but equally certain members of the range such as scarlet, red, etc. In this case the best results are obtained by steaming the printed material in order to develop the Neutrogenes before padding in aniline black.

Mr. R. THORNTON: The lecturer claims in his paper that the Neutrogene dyes have better working properties than the Rapidogens. In view of the fact that both types of dye are chemically similar, is it the lecturer's opinion that these better working properties are a function of the stabilising agent used, and if so what is the explanation for this?

M. JOMAIN: The difference in composition between the Neutrogenes and the Rapidogens is the stabiliser. We think that the properties of the Neutrogenes are essentially due to the better solubility of the stabilising agent used in their preparation. This solubility avoids difficulties encountered with Rapidogen type colours. It is known that with these latter dyestuffs crystals of the stabilising agent incompletely dissolved are sometimes to be found within the print paste, which may cause numerous difficulties during printing.

Mr. W. W. SWORD: The Neutrogene colours appear in my opinion to compare more closely to the Rapid Fast types than Rapidogens, i.e. in respect of neutral developing properties from a caustic alkali print paste. Has the lecturer compared these two colour types in respect of print paste stability and neutral steaming properties?

M. JOMAIN: The Neutrogenes are of course substituted diazo-amino derivatives similar to the Rapidogens, and in this respect are quite different from the Rapid Fast types which are *anti-diazoates*. The stability of the Neutrogene print paste is superior to the stability of the Rapid Fast type of print paste and our new range has of course been specifically prepared to give completely reliable fixation under neutral steaming conditions either alone or alongside vat and other dyestuffs,

Dr. W. SHAW: Neutrogene dyes are chemically similar in character to the Rapidogens, and quite different from the Rapid Fast dyes for which an entirely different method of stabilising the diazo component is used. Nevertheless the Neutrogenes have one feature in which they resemble the Rapid Fast rather than the Rapidogen type of dye, in that many of the series are seriously dulled when they are used alongside aniline black. Is it possible to state why the Neutrogenes should be affected in this way while the Rapidogens are not?

M. JOMAIN: In effect the Rapid Fast and the Neutrogenes behave in the same way towards aniline black, i.e. in general the shades obtained with these dyestuffs are more or less dulled by the aniline vapours. On the other hand, Rapidogens are perfectly suited for printing as coloured resists under aniline black. We think that this difference in properties is due to too slow a coupling speed in the case of the Rapid Fast and Neutrogenes, since if the rate of coupling of the Neutrogenes is accelerated during the course of steaming, it is possible to use certain of these dyestuffs either alongside aniline black or as resists under aniline black. These particular conditions may be achieved by steaming the printed material for a maximum of two to three minutes. The printing

colours having an addition of a small quantity of an acid generator (acid producing salt) such as ammonium sulphocyanide. Under these conditions the Neutrogenes are developed before the aniline vapours are able to dull them to any appreciable extent.

Mr. J. ZONNENBERG: As M. Jomain mentioned in his introduction, tragacanth is not always suitable for these colours under consideration. He gives C.M.C. as alternative, but as we heard from Dr. Krähenbühl's lecture, C.M.C. has poor working properties. I would like to ask M. Jomain if he has any experience with carboxymethyl starch thickening (e.g. Solvitose C) or any other half synthetic thickening to print these colours?

M. JOMAIN: Trials we have made with carboxymethyl celluloses and carboxymethyl starches have given good results from the point of view of *sharpness* and yield. However, the carboxymethyl celluloses have the undesirable property of causing numerous doctor streaks when working with copper rollers and these thickenings are only practicable when using chrome rollers. On the other hand, the carboxymethyl starches do not possess this defect and may be used for Neutrogenes as an alternative to starch tragacanth.

Resists under Azoic Dyes

J. FREI

The introduction of Variamine Blue has given a new impetus to resist printing. The most usual methods—resists by the lead chromate and aluminium chlorate processes—are described, and new possibilities are indicated of producing resists under red, orange, scarlet, and bordeaux diazo components.

Amongst the available processes for producing coloured effects on dyed goods are discharge and resist printing. In discharge printing, white and coloured effects are produced on the predyed goods by local modification of the dye by chemical means, so that the material appears white or coloured after the removal of the decomposition products of the dye. The composition of the discharge paste thus depends on the chemical reaction required from the discharging agent. Depending on the dye used for the ground, oxidising or reducing agents may be used, whilst in some cases acid or even alkaline discharge-printing pastes are employed.

Similarly, in the resist printing technique oxidising or reducing substances can be employed depending upon the type of dye being utilised; in some cases acidic substances alone are sufficient.

A surprising feature of all these recipes is the large quantities of resist agents required to obtain a good effect. We find printing recipes for white resists using 40% tin crystals and 10% tartaric acid, or 60% potassium sulphite. In certain cases, especially with sulphite resists, additions of ammonium tartrate or ammonium citrate were used to increase the purity of the white ground.

For coloured resist styles using basic dyes the resist paste contained 20% tin crystals, 20% tannic acetic acid (1:1) and 20% acetic acid (6° Bé).

These typical printing recipes can be used for white and coloured resists under *p*-nitroaniline→*β*-naphthol by

(1) Preprinting the resist, followed by impregnation and development with a single immersion passage on the padding machine or by overprinting with diazotised *p*-nitroaniline.

(2) Printing the resist on *β*-naphthol and subsequently developing as in (1).

As an early example of resists under azoic dyes let us consider the production of white resists under para red. Here we find that for resist effects on *β*-naphthol under *p*-nitraniline tin crystals were applied mixed with tartaric acid or alternatively potassium sulphite was used sometimes alone or sometimes mixed with substances which had an additional mechanical action. (The value of preprint resists which usually yield a better white than can be obtained by resists printed on the impregnated goods is well known and requires no further elaboration at this stage.)

Printers, generally, preferred sulphite resists to resists with tin crystals because they produced a better white which did not tend to become yellow as was the case with tin crystals and, in addition, did not cause any fibre damage. However, these disadvantages associated with tin crystal resists were overcome when an addition of an organic

acid such as tartaric or citric acid was made to the resist paste.

With the invention of the derivatives of 3:2-hydroxynaphthoic acid the para red style lost much of its importance and, at the same time the resist technique also lost ground.

The discharge method with Rongalite C offered the possibilities of obtaining white and coloured effects on dyed grounds, particularly on the readily dischargeable grounds produced with Naphthol AS red and bordeaux combinations. Furthermore, the discharge method permitted the stocking of large quantities of predyed material which could be discharged when required whilst, in resist printing, it is not possible to work on stock as resist printed goods whether under indigo, vat dyes or diazo compounds generally require a quick finishing process.

Numerous attempts were made to apply the resists possible under para red to the insoluble dyes of the Naphthol AS type but these endeavours were not very successful essentially because of the advantages associated with discharge styles which have been detailed above. However, it is interesting to note a few attempts in this particular field.

One resist which aroused little but theoretical interest at the time was discovered by Oehler and Kallab in the derivatives of hydrazine and hydroxylamine¹, a sulphonated phenylhydrazine being marketed under the name of *Resist H*. Whilst this process referred initially only to the production of white resists under *p*-nitraniline its application was subsequently extended to azoic dyes derived from the arylides of 3:2-hydroxynaphthoic acid².

A white resist using Peralgal OK which gave a pure white with highly substantive coupling components is described by J. Lanzer³ and white resists and half-resists of this type had already been worked out in Japan in 1938 without finding acceptance in industry. On the other hand, Japanese printworks employed white and basic-dyed resists under diazo components, e.g. Fast Red TR and Fast Red KB in which connection tin crystals or tin crystals plus tartaric acid rendered good service.

Formerly blue-red styles were produced on the basis of *β*-naphthol-dianisidine-para red, the dianisidine being printed with persulphate as the resist. With the introduction of Naphthol AS derivatives, red resists could be obtained under Dianisidine Blue, the development bath receiving an addition of persulphate and copper chloride. Dianisidine Blue, however, was inferior in fastness properties, especially in light fastness, to the red combinations and, therefore, was never accepted to any great extent. In addition certain tinctorial

difficulties resulted from the fact that dianisidine is a diamine and, therefore, produces a tetrazo compound when diazotised. Dependent on the conditions and pH of the development bath, this compound may couple with either one or two molecules of Naphtol AS, and this may lead to unevenness as well as shade variations.

The introduction of Variamine Blue, a mono-amino compound overcame the difficulties encountered with dianisidine. Variamine Blue, a *p*-amino-*p'*-methoxydiphenylamine, offers a number of special advantages in printing, for, although the dyeings are easily dischargeable, this product has obtained a good market for resist articles because of its relatively low coupling energy, the low rate of coupling of the diazotised solution, and its sensitivity to acids and alkalis. Excellent white and coloured effects of a bloom and brilliancy not previously known in the Naphtol AS field may be obtained with stabilised diazo components and anthrasols (sulphuric esters of leuco vat dyes).

These prints are obtained by printing on substances which prevent coupling by transforming the sodium naphtholates into free naphthols, which do not couple readily. Amongst such substances are non-volatile organic acids (e.g. lactic, citric, tartaric and glycollic acids), compounds which yield acids on hydrolysis (e.g. aluminium and ammonium sulphates) and reducing substances (e.g. stannous chloride, sodium sulphite, potassium sulphite, and sodium bisulphite). Members of the third group also act by destroying the diazonium compounds in the places printed. The resist agent still further diminishes the already low coupling energy of the diazo component so that the dyestuff cannot form at the places printed.

For resist of articles under diazo components Naphtol AS has the advantage of low substantivity, so that it can be easily removed from the fibre by the customary after-treatment for resist articles. When coupling components of high substantivity are used it is very difficult to obtain perfectly white grounds, the only exception being Naphtol AS-BT (AS-DB) in combination with Fast Red RC, which may be resisted in white with aluminium sulphate and in colours with anthrasols. The white resist effect obtainable with coupling components of high substantivity may be improved by using the preprint resist process. It is possible for instance, by means of this process to obtain white resists with tartaric acid under a grey produced with Naphtol AS-SG and Variamine Blue B. Removal of the naphtholate being preferably carried out with weak caustic soda. It should here be pointed out that, in the resist article, removal of the coupling component from the fibre is as important as removal of the decomposition products from the discharge-printed article.

In Japan for white resist styles under Variamine Blue the preprint process with tartaric acid was preferred and the excellent white resists obtained were reinforced mechanically by the addition of water-repellant agents such as paraffin emulsions. Aluminium sulphate which initially played an important part as a resist agent, was soon abandoned owing to the damage done to the

back cloths by the liberated sulphuric acid. For operational reasons the drying of the resist was carried out on drying cylinders.

For coloured resists under Variamine Blue, diazo components, stabilised diazo components, and anthrasols are used commercially. Amongst the most important processes used in this field are—

- (a) The lead chromate process;
- (b) The aluminium chlorate process.

(a) The lead chromate process has the advantage that resist prints can be produced without steaming. When printing large batches it is occasionally necessary to renew the development bath which gradually becomes contaminated with loose resist compounds, accompanied by formation of lead sulphate.

(b) The aluminium chlorate process is distinguished by requiring neither a steaming nor a hot hydrochloric acid after-treatment to develop the Anthrasol resists and no turbidity or contamination of the development bath occurs in this case. The stability of the Anthrasol printing pastes, originally prepared with aluminium chlorate and ammonium vanadate, was improved by adding the ammonium vanadate to the padding solution. Practical experience has brought about changes in the original process to ensure that the aluminium chlorate forms only when the resists are printed. For impregnation sodium chlorate (20–30 g./litre) is used, and the anthrasol resist containing aluminium sulphate, solvent, and ammonium vanadate is applied as a print-on resist. The formation of the anthrasol dyes, i.e. the decomposition of the acidic resist and the oxidation of the leuco ester by the chloric acid thus released, proceeds when the goods are exposed to the air for about an hour or when the prints are dried on the drying cylinder. It is possible to speed up the development of the anthrasol resists by a short steaming if necessary. Cylinder drying works safely and also permits a further variation—perfect anthrasol-coloured resists may be obtained by adding sodium nitrite and then overprinting white resists. This method of working—bottom printing of anthrasol-nitrite and overprinting of a tartaric acid white resist on impregnated or non-impregnated goods—results, after subsequent cylinder drying, in perfect development of the anthrasol, and was used with much success in Japanese practice because of its simplicity and safety.

Both the lead chromate and the aluminium chlorate processes are used to-day in various countries to produce anthrasol resists under Variamine Blue, either the one or the other process being preferred according to the local operational conditions, as both processes show practically equal results. Incidentally it should be noted that the stability of anthrasol resists prepared by the lead chromate process may be substantially improved by an addition of 1% Rongalite C to the print paste.

Using Variamine Blue B and RT (or BN and RTN) it is possible to obtain a full and bloomy black on a Naphtol AS plus Naphtol AS-G ground and this can be satisfactorily resisted with a mixture of tartaric acid and aluminium sulphate.

This black dyeing is occasionally used for pure rayon and rayon-cotton mixtures and has the advantage, compared with aniline black, of not requiring steaming and of avoiding damage of the material.

The aftertreatment of resist prints requires special care and is preferably carried out on a full width washing machine. After the development and air passage, the goods pass in open width to a series of baths containing sodium bisulphite at 80–90°C. After this hot treatment the goods are then passed through several boiling soap baths containing dispersing agents and are finally rinsed hot and cold before finishing.

In the aftertreatment the uncoupled diazo component adhering to the fibre must be removed and the hot bisulphite baths destroy the excess of diazonium solution but, of course, do not remove the uncoupled, practically colourless naphthol. This is, however, transformed in the soap-soda-ash bath to the sodium naphtholate and this is removed from the goods by a thorough washing treatment at the boil.

Finally, an interesting process for using Variamine Blue resists under vat dyes may be mentioned. It is possible to obtain white resists under vat dyes with calcium nitrobenzenesulphonate. Owing to the fact that it does not dissolve easily this calcium salt has the advantage of not bleeding and thus keeping the resist outlines sharp and free from halos. If these resists to which e.g. Variamine Blue Salt B is added, are printed on naphtholated goods which are subsequently overdyed with vat dyes, it is possible to obtain azoic-dyed resist prints of Variamine Blue under vat dyes. This style which is very interesting from the fashion standpoint and gives fast dyeings was widely represented in the pattern of Japanese summer wear.

After the experience gained with Variamine Blue it was natural to examine how far the other colour bases of the Naphtol AS series were suitable for resist printing. A series of tests were undertaken with stannous chloride, tartaric acid, aluminium sulphate, sulphamic acid and other reducing or acid reacting agents. In general stannous chloride alone was found to be rather unsuitable due to the production of yellowish-white ground shades but when mixed with tartaric acid good results were obtained with a number of red and orange bases. Aluminium sulphate was also found to be suitable, in some cases alone and also in combination with tartaric acid.

When ammonium sulphate and ammonium acetate were examined as additions to the resist pastes, interesting effects were obtained which yielded sharp contours in the printing of dot effects. If a "running resist" consisting of—

- 10% Ammonium acetate
- 20% Ammonium sulphate
- 20% Water
- 50% Starch-tragacanth thickening

is printed on a Naphtol AS padding, dried, steamed for a few minutes in a Mather and Platt steamer and subsequently developed with Variamine Blue Salt B, a uniform light blue bleeding of the blue ground is obtained in addition to a white resist. The addition of ammonium acetate to coloured resists with stabilised or unstabilised diazo components has this same bleeding effect which is always determined by the ground dyeing. Certain other effects may be obtained by mixing coupling components, e.g. by printing a running resist on a Naphtol AS-GR and AS-G ground, in which case development is carried out with Fast Blue Salt BB.

The possibility of using derivatives of phenylhydrazine, owing to their reducing action on the diazo components has already been pointed out. Amongst the numerous available derivatives, phenylhydrazine hydrochloride and phenylhydrazine-*p*-sulphonic acid were examined and, in contrast to all commonly used resist agents, phenylhydrazine-*p*-sulphonic acid has the advantage of being difficultly soluble. In the preparation of white resists the sulphonic acid may be transformed into the soluble ammonium salt by the addition of ammonia. By this process good white resists are obtained under oranges, reds, bordeaux and scarlets. A perfect resist effect is, however, more difficult in the case of Fast Garnet, Fast Brown V and the Fast Black colour salts. Phenylhydrazine hydrochloride is similar in general behaviour to the *p*-sulphonic acid.

As previously detailed, coloured resists with anthrasols can be produced under azoic dyes by the simplified aluminium chlorate process. It is helpful to replace part of the aluminium sulphate in the resist printing pastes with phenylhydrazine-*p*-sulphonic acid, which results in a clear anthrasol resist which is hardly influenced by the diazo solution during development. The use of phenylhydrazine derivatives in the production of white and coloured resists with anthrasols under red diazo components has already been introduced in the U.S.A. The patent situation of this resist process is not yet entirely clear and therefore no further details can be given at present. That this resist process satisfied all printing conditions may be seen from the printed patterns shown, which are taken from the American industry.

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(MS. received 21st April 1953)

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Discussion

Mr. R. J. HANNAY: Can the lecturer tell us if there are any toxic effects or dangers to workmen in the use of phenylhydrazinesulphonic acid? It is well known that the use of hydrazine salts such as hydrazine sulphate does present toxic hazards. Is phenylhydrazine sulphate different in this respect?

Dr. FREI: From experience in the U.S.A. we can say that no bodily damage to workmen has been observed. We know that phenylhydrazine or its derivatives possess poisonous properties to a certain extent, producing dermatitis, or destroying the red blood corpuscles. Consequently, when working with these products special care and precautions should be taken as a protective measure against the disadvantages of these products.

Dr. E. A. KRÄHENBÜHL: There is indeed a very strong objection against using aluminium sulphate "as is", but I have in my practice very good experience in printing white resists under Variamine Blue even in extended areas without fibre tendering on goods or back greys when employing aluminium oxide neutralised with soda ash until Congo Red paper does not turn blue any more. I should like to ask the lecturer whether the new resists he recommends offer a substantial advantage over neutralised aluminium sulphate, because there is a serious price question and any organic compound like phenylhydrazinesulphonic acid would not be competitive against the very cheap aluminium sulphate.

Dr. FREI: I should like to point out that it is not our intention to replace aluminium sulphate by phenylhydrazinesulphonic acid. For resist prints under Variamine Blue aluminium sulphate works very well, and is very effective, as is aluminium sulphate neutralised with soda ash. For several reasons, however, printing factories in Japan preferred to use tartaric acid, which was imported from Italy at a rather low price. It goes without saying that phenylhydrazinesulphonic acid is recommended only for the production of white resists under red, scarlet, orange, or bordeaux azoic compounds. When, for instance, in such cases a good and reliable white resist can be obtained with tartaric acid + stannous chloride, it is advisable to work with these products. Should any difficulties arise the use of phenylhydrazinesulphonic acid is recommended.

Herr L. POLESIE: I would like to know if these resist prints can be used also for screen printing?

Dr. FREI: These resist prints can be used for screen printing. In this case it is advisable to vary the quantities of the resist printing agent. Half the quantity used in machine printing should be sufficient when the screen printing method is used.

Mr. F. CROMPTON: In England the practice is to dye with a dyeing machine following the printing machine to avoid marking off. Does the lecturer advise this method?

Dr. FREI: When resist printing it is advisable to pass the goods in full width through a padding machine with a colour box containing the developing liquor. The goods are then squeezed and given an air passage, followed by a treatment in open

width in sodium bisulphite solution. This passage must be made long enough for all the uncoupled diazo compound left in the fibre to be destroyed. The goods are then rinsed, treated again in a second bisulphite bath, rinsed again, treated with water in rope form, and finally soaped at the boil.

Mr. W. TAUSSIG: What is the advantage of the resist printing method, when producing such large white motives as displayed by the lecturer, compared with a "trough print" using the direct printing method, as applied so frequently for African styles in this country?

Dr. FREI: Strictly speaking, we cannot compare a resist print with a direct print. In many cases it is the customer who wants a print produced by the resist printing method with a two-sided dyeing effect. This effect cannot be simply produced by ordinary direct printing methods. It is also the resist printing method by which especially large white motives can be produced in an absolutely clear white effect without any difficulties. Direct prints can be made more cheaply, but in many cases the penetration often leaves very much to be desired, and the white is often stained. The degree of washing out of the Naphtolate depends on the kind and quality of the goods, on the method of Naphtolating, and on the kind, or substantivity, of the Naphtol itself.

The articles I showed have a long historic development, and were originally produced by the Japanese "pump dyeing" method with indigo. By this method an excellent white and an excellent solid ground dyeing on both sides of the goods could be obtained. The taste of the Japanese customer has not changed for some centuries, and remains unchanged to-day.

It was not possible to get the required effects by direct printing methods, and therefore there is only one method left for producing this article—the resist printing method.

Mr. HANNAY: The choice of resist printing methods is frequently favoured by the necessity for the production of prints which are reversible in effect. It is much more difficult to produce direct prints in which the ground colour is as solid on the back of the fabric as it is on the face. Heavy engravings, and high pressures are required on the printing machine, and the balance between prepare and the diazo coupling component has to be carefully controlled. Resist methods provide a simpler method of producing a solid ground on both the face and back of the fabric.

Mr. L. A. DRIESSEN: A further reason for producing resist prints instead of direct prints is that for many export articles the resist is wanted by the customers.

Mr. R. THORNTON: The question under discussion, as to whether it is desirable to produce a white effect on a navy ground by a resist or a direct printing technique, appears a little confused. The fact that the prints in question have been produced in Japan tends to exclude a direct printing technique for a navy blotch, because the printing machines normally employed use a rubber bowl in place of the conventional steel bowl with lapping, blanket and backgrey.

New Developments in the Application of Phthalocyanines in Textile Printing

F. GUND

A completely new method of using phthalocyanines in textile printing was introduced by the discovery of the Phthalogens, from which the phthalocyanine pigment may be produced in the fibre. Special methods of application were developed, which are characterised by the use of 10–20% of special solvent mixtures, the Levasols, in the aqueous printing pastes containing the intermediate product and the metal, the latter in the form of a soluble salt or as a complex compound.

The printing method is adapted to the usual processes and apparatus used in textile printing. Particular attention must be paid to the drying of the prints and pads. Condensation to the dye is best carried out by steaming.

The printing process with Phthalogen Brilliant Blue IF3G, the intermediate product, which with a copper salt or the copper complex compound Phthalogen K gives very bright blues of high fastness to light, weather, and boiling, and with nickel salts greenish blues of equally high fastness properties, is described in detail, and the solubility and the stability of the intermediate product are discussed. The possibility of printing alongside dyes of other groups is considered.

Success has recently been achieved in developing a process for the production of white and coloured resists under Phthalogen Brilliant Blue IF3G, the resisting agent being an organic base (Phthalotrop B).

The production of a green phthalocyanine pigment on the fibre has been made possible by the manufacture of the intermediate product Phthalogen Brilliant Green IFFB. The printing process is similar to that used for the production of the blue dye. The lower solubility of the intermediate product requires the use of another solvent, Levasol F, and the dispersing agent, Emulsifier W. Owing to its extraordinary brightness and outstanding fastness properties, the dye containing copper is of greater importance, the copper being applied as Phthalogen K. The method of printing is discussed, as well as the possibility of application alongside other dye groups in direct printing.

Phthalocyanine Dyes

After the introduction of the phthalocyanine pigment, Monastral Blue (ICI) or Heligen Blue, when the outstanding features which distinguish the phthalocyanine ring system were recognised, considerable research was devoted to making this group of substances suitable for the dyeing of textiles.

To mention only those products which have been of technical value, milestones along this road have been the dyes Sirius Supra Turquoise Blue GL (IG), Alcian Blue (ICI), Sulphogen Brilliant Green I (DuP) or Thionol Ultra Green B (ICI), Indanthren Brilliant Blue 4G (FBy), Phthalogen Brilliant Blue IF3G (FBy), and Phthalogen Brilliant Green IFFB (FBy). With the exception of the sulphur dye, all these products have acquired importance for the printing of textiles. In this paper, only the three last-mentioned dyes, marketed since 1949, will be discussed in detail.

Sirius Supra Turquoise Blue GL is a phthalocyanine derivative rendered water-soluble by the introduction of sulphonyl groups. It shows substantivity, but only moderate wet fastness properties.

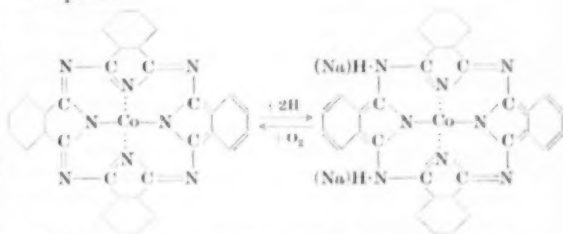
In Alcian Blue we have a water-soluble derivative of phthalocyanine, the solubility of which is based on quaternary ammonium groups. When developed in steam, these solubilising groups undergo a chemical change on the fibre, so that the dye is fixed in an insoluble form.

The chemically interesting synthesis of Thionol Ultra Green B, which is soluble in sodium sulphide, enriched the range of sulphur dyes by a shade similar to that of Caledon Jade Green, showing high fastness to light and, for this group of dyes, unusual brilliance, but only moderate fastness to chlorine and boiling.

INDANTHREN BRILLIANT BLUE 4G

Shortly after the introduction of Alcian Blue, Indanthren Brilliant Blue 4G appeared as a further

textile dye of the phthalocyanine group. In the case of this phthalocyanine, containing cobalt as the central metal atom, the interesting discovery was made that, as in the case of a vat dye, it could be converted to a reduced soluble form. Alkaline reducing agents, preferably in the usual caustic soda-hydrosulphite vat, yielded a kind of leuco compound—



Although the reducible quinone groups typical of vat dyes are not present in the molecule, displacements presumably occur in the quinonoid bonds of the phthalocyanine ring system under the influence of the reducing agent, so that the molecule is able to take up hydrogen atoms which can be replaced by alkali, i.e. this hydro compound can be ionised.

Until recently, this dye was recommended only for dyeing purposes¹, and in this form was not generally suitable for printing purposes. Sufficient fixation could be obtained only by the continuous method of development of the Colloresin process. Adequate fixation could not be obtained by the Rongalite-potash process. By the use of certain auxiliary products it has now been found possible to market this dye in a form which is suitable also for printing with potash-Rongalite.

INDANTHREN BRILLIANT BLUE 4G PASTE FOR PRINTING

Amongst the fastest-to-light blue vat dyes Indanthren Brilliant Blue 4G is outstanding for its

remarkably pure greenish shade. Owing to its poor fastness to chlorine, however, the field of application of this dye is limited. On the other hand, its fastness to washing and boiling is superior to that of the halogenoindigos. This product should be of interest, for example, for articles made from filament or staple viscose rayon, for which fastness to chlorine is not required. The dye shows normal stability as a printing paste, but it is advisable to steam the goods soon after printing. Their tinctorial strength deteriorates appreciably if the prints are left under unfavourable conditions for some little time prior to steaming. Although this dye can also be combined with other vat dyes, the bright self-shade should be of the greatest interest. Reference may be made, however, to the shading possibilities with Indanthren Brilliant Violet and the Caledon Jade Green (ICI) brands.

Phthalogen Brilliant Blue IF3G

The compound which will now be discussed is not a true dye but a special intermediate product which permits the production of the phthalocyanine-metal complex as a pigment in the fibre.

GENERAL REMARKS

A historical survey of the evolution of methods of textile printing, which has resulted in great improvement in the general fastness properties of printed textiles, will reveal cases which are similar to the present Phthalogen process of development, and may be of assistance in understanding the technical principle involved and the points to be observed.

The development of fast textile printing is characterised by processes which have aimed at producing insoluble dyes from intermediate products on the fibre. The production of Aniline Black, α -nitroso- β -naphthol-metal complexes, and insoluble azoic dyes on the fibre may be mentioned as examples. In all these cases, the synthesis of the dye, whether in the first stage, as with oxidation blacks, or only in the last stages, as with the nitroso- β -naphthol-iron complex or the azoic couplings, is placed in the hands of the user, and must be carried out on the fibre at the actual printworks. The fibre may be considered in these cases as a reaction vessel, whilst itself being a structure capable of undergoing chemical reaction. Thus only reactions which under favourable conditions proceed smoothly, and where the course of the reaction is limited to the intermediates themselves, without involving the fibre, can be carried out successfully on the fibre. In addition to physical requirements, such as solubility and similar powers of penetration of the components involved in the reaction, high reactivity is an important item in dye syntheses on the fibre. In some cases, catalysts must be used to accelerate the reaction. High reactivity is, of course, associated with limited stability, as in the cases of azoic diazo components.

In this survey of the older methods of textile printing, we must consider both the simpler processes, which are practically uninfluenced by secondary reactions and therefore take place with a high colour yield (e.g. azoic coupling and simple metal-complex compounds of nitroso- β -naphthol),

and the more complicated reactions in the formation of Aniline Black. Some led in practice to many difficulties, chiefly of a physical nature, in spite of simple chemical conditions (e.g. azoics), whilst others were satisfactorily mastered in the course of time, despite complicated chemical processes (e.g. Aniline Black).

In the case of the phthalocyanine synthesis from Phthalogen Brilliant Blue IF3G, the conditions, from a chemical point of view, are simpler than in the case of the Aniline Black condensation, but by no means so simple as in the case of azo coupling. Above all, it must be remembered that we are dealing in this instance with the production of one of the purest shades which dye synthesis has been able to produce. When these circumstances are taken into account, it seems remarkable that the synthesis of the phthalocyanine can be carried out on the fibre to yield such good tinctorial strength and purity of shade.

The first essential features were the discovery of the excellently reacting intermediate product itself—Phthalogen Brilliant Blue IF3G—and the formulation of a suitable solvent mixture as a medium for the condensation reaction. In addition, it was necessary to adapt the proportions of solvent to the intermediate product and the latter to the metal salt, and, finally, to gain a knowledge of the other conditions which determine the course of the reaction. The solution of this task is due to the co-operation between the chemists engaged in scientific research and the joint work of these chemists with the dyeing experts of the user plants. A great deal of experience gained in actual practice was used as a basis for printing recipes and development methods before the product was offered to the trade, and, as generally occurs with new developments, a certain standard was attained. The work of improving the application of this product continued, however, so that to-day, after about two years of actual practice, with a modified solvent and a complex copper compound, further progress has been made towards increased reliability in the application of this dye.

Phthalogen Brilliant Blue IF3G has now been used in bulk in a number of the most important printworks in Europe and is in constant use. Experience has proved that the requirements for a constant and reproducible result are more easily fulfilled in actual practice than was expected from tests made in the laboratory. The procedure for the preparation of the dye for printing purposes will now be discussed in detail.

INGREDIENTS OF THE PRINTING PASTE

Intermediate Product

(Phthalogen Brilliant Blue IF3G)

In the dry state this physiologically harmless basic intermediate product, which is marketed as a finely ground powder, possesses good stability.

Solvents

These are marketed under the designation *Levasol*. They are mixtures of liquid organic compounds of high boiling point, which are miscible with water. The mixtures show a basic reaction; the character of a dihydric alcohol predominates.

Two products can be used for printing Phthalogen Brilliant Blue IF3G—Levasol P and Levasol PO. The formulation of the respective mixtures was determined empirically by the evaluation of prints. There are many possibilities of formulating suitable mixtures, but Levasol P has proved to be the best possible mixture with regard to yield and brilliance of shade. This has been confirmed in actual practice and, at present, no superior mixtures have been discovered.

Owing to the organic amine content, both the solvents mentioned should, as far as possible, be prevented from coming into contact with the human skin. Tests have shown that inhalation of the vapour of Levasol P is not particularly harmful. The vapour has, however, a sweetish, pungent odour which many people are unable to tolerate. In any case, it is advisable to make adequate provision for the removal of the Levasol vapour, the presence of which is marked on drying, more marked on steaming, and most marked of all during thermal condensation.

There have been many attempts to formulate the solvent mixture in some other manner in order to mitigate the inconvenience caused by the vapour. To a certain extent, this has been accomplished in the product marketed as *Levasol PO*, which will be discussed later in connection with Phthalogen Brilliant Green. A third mixture, the formulation of which is intended for this country, predominantly from British products, would behave still better in this respect.

All these mixtures possess unlimited storage life. They attack zinc, copper, and copper-containing metals, but containers made from iron and aluminium are not attacked. Up to the present, the solvents have been despatched in glass vessels.

Compounds supplying the Central Metal Atom

Dyes of interest for textiles are obtained with copper or nickel as the central atom. The usual salts of these metals—copper sulphate, copper chloride, copper acetate, nickel chloride, and nickel sulphate—can be used. In the production of the copper complex it has been found that copper chloride shows a slightly better colouring power than the sulphate.

In the preparation of the printing paste, it has been found necessary, in order to obtain the purest shade, to use less than the stoichiometric quantity of the metal salt. If the dye condensation is carried out properly, the metal combines completely and is firmly fixed in the dye molecule, but when the quantity of metal salt used exceeds this optimum, a duller and greener shade is likely to result, with, however, no increase in tinctorial strength. The metal ions (copper or nickel) are converted into complex compounds on contact with the basic Phthalogen Brilliant Blue IF3G and the amine-containing solvent, and it is presumed that the monomeric intermediate product is predominantly concerned in this primary complex formation. Higher complexes containing the metals, the first steps towards the dye, form only very slowly in the printing pastes at low temperatures.

Within the limits indicated in the printing recipes, the quantities of metal salts may be varied,

depending on the material to be printed and the drying and steaming conditions; the most favourable quantity should be ascertained on each occasion by a large-scale trial. In addition to the metal salts which were exclusively recommended at the outset, a specially produced metal complex compound—Phthalogen K—can be used to advantage.

Adjustment of the pH

Ammonium acetate has proved suitable as a buffer.

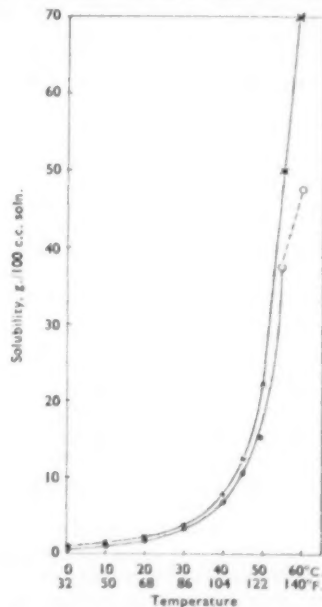
PREPARATION AND BEHAVIOUR OF THE PRINTING PASTES

A full-depth printing paste which is thickened with tragacanth has, on the average, the following composition—

Solid substances	...	9.11%
Solvents	...	14.20%
Water	...	77.69%

In the printing paste the aqueous medium therefore predominates.

The content of solvents must not be below 10% even in the case of reductions. The solvent mixture has to serve as a medium for the condensation reaction on the fibre after printing and drying, but it also promotes the uniform penetration of the ingredients of the printing paste into the fibre during the printing and drying operations. Consequently, the penetration and the fastness to rubbing are generally increased by using an increased quantity of Levasol. In spite of the high boiling point of the individual components, part of the solvent mixture will evaporate during the drying, as the steam volatility of the mixture is higher than that of the individual components.



(i) —x— Determined by weighing
(ii) —○— Determined by titration with 0.1N-HCl

FIG. 1—Solubility of Phthalogen Brilliant Blue IF3G in Water

The solubility of the intermediate product in water can be seen from Fig. 1, the two curves being based on two different methods of determination. In one case (i), the difference between the analysed sample and the undissolved residue was ascertained, whilst in the other case (ii) the base which had been dissolved was determined by titration with hydrochloric acid. The agreement is good. The solubility increases gradually up to about 86°F. (30°C.), and then steeply until very high values are attained. At low temperatures, which are of particular interest to us, the solubility is limited, being approx. 20 g./litre at 68°F. (20°C.). In Levasol P and PO the solubilities at 50°F. (10°C.) are about 15 and 10 g./litre respectively, whilst at 68°F. (20°C.) the values are only a little higher. In the mixture of Levasol and water solubility at low temperatures is very much higher. Thus, 50 g. of the intermediate product can be dissolved in 150 g. of Levasol P plus 75 g. of water at 68°F. (20°C.).

In the preparation of the printing paste, the copper or nickel salt solution or a 10% solution of Phthalogen K is added to the intermediate product pasted up with Levasol. On addition of the metal salt solutions, a finely precipitated paste is obtained; whilst on addition of the Phthalogen K solution, a clear olive-green solution results. This difference in appearance is presumably due to the fact that in the first case an intermediate copper complex which is less freely soluble in the Levasol mixture is formed with the monomeric intermediate product, whereas this does not occur with the co-ordinated copper in the Phthalogen K.

Stability

The intermediate product shows a limited stability in aqueous solution. It undergoes hydrolysis with the evolution of ammonia. The rate of hydrolysis depends to a large extent on the temperature (Fig. 2). The amount of unchanged base was determined at regular time intervals by

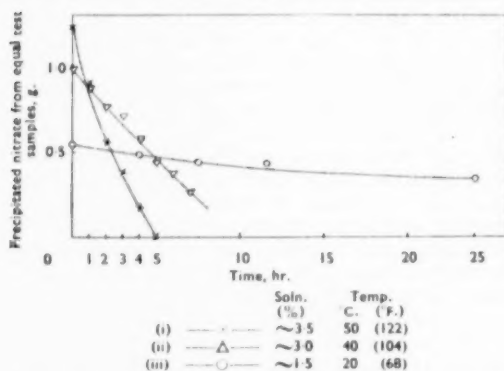


FIG. 2.—Rate of Hydrolysis of Phthalogen Brilliant Blue IF3G in Water

weighing the nitrate of the base, which could be isolated quantitatively by precipitation. In this case, the concentrations at the various temperatures were so selected that in each instance they lay below the point of saturation, precipitation of addition products of the product of hydrolysis and

the unchanged starting material, which would have led to incorrect results, thus being avoided. After 5 hr., the loss of base due to hydrolysis amounts to 13% at 68°F. (20°C.), 55.1% at 104°F. (40°C.), and 100% at 122°F. (50°C.). From curve (iii) it can be seen that the loss at 68°F. (20°C.) after 24 hr. amounts to 37%. The data for solutions at lower temperatures are not available, but the rates of hydrolysis are correspondingly lower.

The stability of Phthalogen Brilliant Blue IF3G was also tested in the printing paste (tragacanth thickening) by a comparison of the prints obtained after standing for definite periods. In order to preclude variations due to different drying and steaming conditions, the prints which were to be compared were all produced at the same time with printing pastes which had been prepared at different times. These stability tests at different temperatures showed that decomposition depends to a great extent on the temperature. At 50°F. (10°C.) no perceptible decrease of tinctorial strength was observed after 24 hr.; at 68°F. (20°C.) there was a noticeable decrease after 8 hr.; whilst at 86°F. (30°C.) the tinctorial strength had decreased after standing for only 3 hr. Practical experience has shown that, when cooled below 50°F. (10°C.), e.g. in a refrigerator, the printing pastes can be used for several days. The printing pastes can therefore be prepared in larger quantities, ice being used if necessary; they are then kept cool, and supplied to the printing machine in small quantities as required. It is also advisable to cool the colour box, although losses due to heating of the colour box can be kept low without cooling by reducing the contents of the box as much as possible and adding the cooled printing paste at shorter intervals. Residues are replaced in the refrigerator and used, if desired, strengthened by the addition of a corresponding quantity of Phthalogen Brilliant Blue IF3G dissolved in a little methanol, or they may be used for reductions.

Compared with hydrolysis, premature condensation to the dye is relatively unimportant as a cause of limited stability. In principle, however, the printing pastes should be protected from the influence of light in order to prevent premature condensation.

In the strengthening of printing pastes in which hydrolysis has occurred, an addition of metal salts is, of course, unnecessary. No advantage as regards stability is gained by adding the metal salts just before use. This method is not advisable because in this way it is impossible to obtain smooth printing pastes.

Printing pastes containing nickel salts are also subject to decomposition, although not quite to the same extent as those containing copper.

An increase of the absolute quantity of Levasol in the printing paste within the limits indicated exerts no vital influence on stability. For reasons of economy an increase to above 20% of solvent cannot be considered.

Selection of the Thickening Agent

When these products were first introduced, tragacanth was the chief thickening agent recommended. This thickening agent produces on the

materials normally printed the most level prints coupled with good tinctorial strength and fastness to rubbing. Numerous natural and industrially prepared thickening agents may, however, be used, provided that they do not cause precipitation of the metal salts and are not flocculated by the solvents. Thus, for example, alginates and cellulose ether carboxylic acids are not suitable for printing pastes when copper or nickel salts are used. Cellapret (sodium carboxymethyl cellulose) is quite compatible with Phthalogen K. This thickening agent shows a good colour yield on rayon staple. Thickening agents having reducing properties, such as British gum and dextrinated starch, cannot be recommended, as the tinctorial strength and the shade are adversely affected. The pure starches in general use for thickening purposes give increased tinctorial strength together with inferior penetration. They are therefore superior to tragacanth as regards intensity and, to a certain extent, as regards brilliance of shade. By a combination of starch and tragacanth it is possible to select the most favourable middle course with regard to evenness of the prints and tinctorial strength, depending on the conditions imposed by the nature of the goods and the pattern. Where starch is used alone or in combination with thickening agents which can be washed out, proper attention must be paid to a thorough removal of the starch by malting, otherwise the fastness to rubbing will not be of the desired standard.

Locust-bean gum may also be used, but the typical gum thickenings, including crystal gum, give weaker prints.

TEXTILES ON WHICH PHTHALOGEN BRILLIANT BLUE IF3G CAN BE USED

The field of application can be briefly described—Natural and regenerated cellulose fibres are suitable. Acetate rayon must be excluded at present, as on this material it is impossible to obtain sufficient fixation. On wool and silk much weaker and less brilliant shades are obtained.

With the recipes given at the outset, the best results with regard to tinctorial strength and brilliance of shade were obtained on cotton, particularly mercerised cotton, and on cuprammonium filament rayon.

On viscose filament and staple rayon the tinctorial strength with the respective printing recipes decreased sharply, and the desired redder shade obtained on cotton could not be achieved. An improvement was soon obtained. By means of empirical tests it was ascertained that an addition of ammonia to the printing paste considerably increased the tinctorial strength on viscose rayon, and, following up these observations, Levasol V was tested. At a high concentration this solvent must not come into contact with the intermediate product, as it would react with the latter, forming substitution products which could no longer be condensed. Levasol V can therefore be used only as a final addition to the prepared printing paste. In a further investigation of this problem, a product was finally found which did not show the inconvenient reactivity of Levasol V, the result being

Phthalogen K, in which the copper is bound in a relatively stable complex. Compared with copper salts and a Levasol V addition, Phthalogen K offers distinct advantages in the printing of viscose filament and staple rayon as regards tinctorial strength and shade. Above all, the results are more reliable and can be more satisfactorily reproduced than by the use of Levasol V.

The following hypothetical explanation may throw light on the mode of action—Rayon staple fibre presumably offers greater resistance than does cotton to the diffusion of the intermediary Phthalogen Brilliant Blue IF3G-copper complex, so that after the prints are dried the components necessary for the formation of the dye are not present in the rayon staple in the correct proportions. The improvement obtained by the use of ammonia leads to the conclusion that in this case the formation of the difficultly diffusible Phthalogen Brilliant Blue-copper complex is at least partly prevented, and that the cuprammonium complex formed in its place diffuses more easily into the fibre. Levasol V also is able to form complex copper compounds, the mode of action being similar to that of ammonia. With Phthalogen K, however, an even closer approach is obtained to the best conditions for viscose rayon. Tests carried out in practice have already confirmed that by the use of Phthalogen K on viscose rayon a considerable increase in the colour yield is achieved, whilst the same reddish shade as on cotton can be obtained with greater reliability than by the use of Levasol V.

As regards Phthalogen Brilliant Blue IF3G prints on viscose rayon staple, it must also be pointed out that the pretreatment of the material may exert an important influence on both the shade and the tinctorial strength of the prints. We have ascertained that too flat or too dull prints could be ascribed to some by-product in the fibre, which should have been removed by pretreatment in a hot scouring bath made slightly alkaline with soda.

In the case of the Phthalogen Brilliant Blue-nickel complex dye there are also differences in tinctorial strength on the various cellulose fibres, but the difference in strength between cotton and viscose rayon staple is less pronounced than in the case of the copper dye. No nickel-phthalocyanine complex has yet been marketed for improving the tinctorial strength on rayon staple.

PRINTING METHODS

Roller printing and screen printing are used for direct prints. In single-colour roller printing no difficulties have arisen in the actual printing. Even where non-chromed printing rollers are used, no adverse effects of the printing pastes on the roller and no deterioration of the Phthalogen Brilliant Blue-nickel dye, which might result from the dissolution of copper, have been observed.

In screen printing, attention must be paid to the swelling or dissolving action of the solvents on the screen lacquer. From the numerous lacquers on the market a suitable selection should be made for the screens, a lacquer which is resistant to organic bases being chosen. In our opinion, the most resistant

lacquers are those based on thermosetting plastics. The table covering must also be resistant to the solvents. In this respect, table coverings made of rubber appear less suitable, although no actual complaints have been received concerning them. Table coverings on a plastic basis resistant to solvents and also oilcloth appear suitable. Attention must also be paid to the nature of the adhesive which may be used to hold the goods on the table. Products showing a reducing action, such as dextrin, may adversely affect the tinctorial strength of the prints from the back, and in this way give rise to stains.

In screen printing it is also advisable to exclude strong light whilst the goods are being printed. Printing pastes containing nickel, in particular, are sensitive to the influence of light whilst in a wet condition on the table. This results in greener and duller prints.

Printing on heated tables is possible, but for fundamental reasons (see below) drying with hot air appears to be a better method.

DRYING OF THE PRINTS AND PADS

Drying appliances in the finishing of piece-goods are mostly designed with the object of obtaining the highest possible efficiency in the removal of water. Even in the most modern drying systems this is the chief aim. When drying is carried out at an unstable intermediate stage, however, the object of the quickest possible removal of water must necessarily be subordinate to other considerations resulting from the physical or chemical behaviour of the intermediate product which is being dried. The physical problem of the prevention of migration phenomena due to local differences in the speed of drying is well known. This is particularly important in the padding of Phthalogen Brilliant Blue IF3G, in which we are interested mainly for the production of the resist style, which will be discussed later. In addition to the migration of the components of the printing paste, we are also interested in the behaviour of the solvents, the hydrolytic decomposition of the starting material, and the precondensation of the Phthalogen Brilliant Blue IF3G, all of which can be affected to a certain extent by drying. On the whole, it must be recognised that the processes occurring in drying are extremely complicated, but a study of the behaviour of the ingredients of the printing pastes gives some information which will serve as a guide in controlling the course of the drying process.

Owing to the tendency of the intermediate product to hydrolytic decomposition, which, as we have seen, increases considerably with rise in temperature, the problem is to remove the water as rapidly as possible without the film of printing paste on the goods becoming too hot whilst water is still present. In practice, this means a good circulation of air in hot air chambers or hot flues, and good ventilation and quick running in cylinder drying. So long as the removal of the water vapour is in the correct ratio to the supply of heat, the goods themselves will not show excessive, harmful temperatures before the dry state is approached. As the reaction of hydrolysis requires time, however, the competition between removal of water and

increased hydrolysis due to higher temperature is more in favour of the former process the quicker the water vapour is removed by an abundant supply of dry air. It may be presumed that, even where drying is properly carried out, certain losses take place as the result of hydrolytic decomposition. Such losses compared with the theoretical colour yield are unavoidable.

When the removal of the water in drying comes to an end, the resultant considerable rise in temperature causes the start of condensation to the dye, which takes place in intermediate stages. As the building up of these intermediate products proceeds, they lose their tendency to hydrolyse. It can also be presumed that with increasing concentration of the solvent the tendency to hydrolyse is diminished.

Another point which merits attention in controlling the drying conditions is the volatility of the Levasol components themselves, particularly in steam. A partial evaporation of the organic solvent might occur if great heat were suddenly applied, for instance on very hot drums or in nozzle driers. In view of this, a middle course should be taken, which has proved suitable for the intermediate drying of Phthalogen Brilliant Blue, viz. drying at ambient temperatures of about 176°F. (80°C.) with good air circulation.

Under these conditions, most goods can be completely dried after about 10 min. in the drying chamber or hot flue, without undue evaporation of the solvent. We have observed in actual practice that, when the drying temperature is too low, the colour yield obtained is likewise too low. Drying in moderately warm suspension drying rooms is also, of course, unsuitable. In large-scale production, drying cylinders have given good results. This method of working is not usual on the Continent, and we have therefore had little opportunity of gaining experience in this connection. We presume, however, that by regulating the heat supplied to the drum in accordance with the speed of rotation equally good results should be obtainable as by the above-mentioned method of hot-air drying at 176°F. (80°C.).

In the drying of paddings for solid shades and resists the same rules apply as given above, but in view of the danger of migration, particular attention must be paid to the apparatus, as it is essential to dry the fabric uniformly in all parts. The goods must lie flat and in open width, as otherwise uneven drying will occur in the folds, and streakiness and differences in tinctorial strength will at once become apparent.

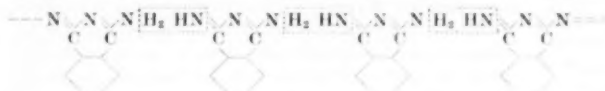
Tenter-frames are not unsuitable, but marks are made by the clips and pins. The best arrangement is a hot flue, for uniform drying at the sides and edges can be ensured by guiding the stream of hot air. Drying by means of hot air nozzles is possible, provided the temperatures used are not excessive. Cylinder drying can be used for plain goods, but irregularities, such as burls, become apparent in the finished dyeing. Naturally, raised interlacing effects also show up in cylinder drying. The temperature of the drying drums should not exceed 212°F. (100°C.), and a sufficient number of drums

must be available for the work to be carried out rapidly. It has been found in actual practice that on drums the danger of migration can be obviated by submitting the fabric beforehand to a short hot-air drying, so that part of the water is removed before the goods reach the drums.

THE CONDENSATION

After drying, the greater part of the solvents remains on the goods. In addition, the phthalocyanine, presumably already in a condensed polymeric form with partly bound metal, portions of the unchanged intermediate product, part of the metal in its original form in the printing paste, and, of course, hydrolysis products are present. The dye itself, however, is developed only to a slight extent. Full development requires a greater supply of heat, and this can be applied by several methods, such as radiation, contact, hot air, or, last but not least, steam.

In addition to the condensation of four molecules of the Phthalogen preproduct to the phthalocyanine ring system, there is another possibility of reaction, which presumably leads to the formation of open chains of several *isoindole* residues—



These by-products cause a certain discoloration of the shade, and can readily be removed by acid treatment.

The presence of moisture is not absolutely essential for the development of the dye. Single-coloured designs can be developed in dry heat for 2–3 min. at 248–266°F. (120–130°C.). Cylinder units arranged so that the goods are dried alternately on each side, as well as condensation apparatus of the kind used for the crease-resist process, are suitable for this purpose. In works practice, however, where the illuminating colours must also be considered, steaming is the normal method of fixation. The reaction leading to the development of the blue dye proceeds rapidly in steam, the final result being obtained in most cases after a few minutes. At all events, no appreciable differences in the colour yield are perceptible between prints steamed for 5 and 10 min. respectively.

Given good steaming conditions, the results as regards colour yield are in no way inferior to those obtained with dry heat. Small-scale tests have shown, however, that, compared with saturated steam, up to 15% increase in colour yield can be obtained in dry steam at 226–230°F. (108–110°C.). Reports from the trade regarding the assessment of the influence of the steaming conditions (qualitative) do not in all cases coincide. Whilst satisfactory results are mostly reported with ordinary steam, or possibly rather less wet than is preferred in many cases for vat dyes, it has also been stated in other quarters that, particularly on rayon staple, improvements in comparison with dry steam have been obtained with very wet steam, or even by spraying with water immediately before the goods run into the steamer. In view of the important rôle

played by the drying with regard to the colour yield, we are inclined to think that different assessments in respect of steaming are really due to differences in the drying. In the case of rayon staple, there is also the previously mentioned uncertainty which has only recently been obviated to a large extent by Phthalogen K (copper complex). Indeed, a true evaluation of the developing conditions as regards the optimum colour yield can be obtained only by systematic, exact tests in which the variables which determine the tinctorial strength, above all the speed and the temperature of drying, are kept constant and near their optima. The experience gained to date makes it clear that, although somewhat elevated steam temperatures are an advantage, variations during steaming are not nearly so important as variations during drying.

In view of the use of Rapidogen dyes as illuminating colours, the behaviour in acid steam also deserves some mention. In this case the tinctorial strength depends upon the acid concentration of the steam, and is diminished when the latter is very high. By a corresponding reduction of the acid concentration, in conjunction with a certain reduction of the quantity of caustic soda in the

Rapidogen printing pastes, prints which are practically as heavy as those obtained in neutral steam are ensured.

All the influences which have an adverse effect upon the tinctorial strength, such as unfavourable drying, steaming conditions, and acid steam, are particularly apparent in the case of reductions. This is due to the fact that dilution of the reactants retards the condensation reaction, whilst it increases the tendency to hydrolytic decomposition, in accordance with the law of mass action. Hydrolysis can be counteracted by particularly effective drying and additional quantities of Levasol.

In principle, there are no differences between nickel and copper complexes with regard to the condensation reaction. The nickel complex does not form as completely in acid steam at higher acid concentrations as in neutral steam, particularly when reductions are being developed.

THE ACID AFTERTREATMENT

When the dye has been developed by dry heat or steam, the prints or pads have not yet attained their final colour. The removal of the thickening and the soaping at the boil also do not produce the final colour, and this difference is particularly noticeable in the case of the copper dye, although the nickel dye shows similar characteristics. The deviation in colour is one of degree, depending on the nature of the goods and the conditions of development, the colour being generally duller and greener. These discolorations are due to by-products formed during condensation, and are eliminated by an acid aftertreatment. This can be carried out with 5 g. oxalic acid plus 5 g. formic acid (85%) per litre in an almost boiling bath for 10 min. Almost the same result is obtained, however, by an aftertreatment with hydrochloric acid or sulphuric acid, in which case 10–20 c.c. per litre is used. This aftertreatment with mineral acid is suitable for continuous working, as at 185–194°F.

(85–90°C.) the clearing effect is obtained in 20–30 sec. In the production of the copper phthalocyanine, using Phthalogen K, the colour from the start is considerably brighter than that obtained by the use of copper salts, so that the pure hue of the dye is particularly easy to obtain by means of the acid aftertreatment. In cases where, owing to the illuminating colours being sensitive to acid, an acid aftertreatment cannot be given (e.g. in the case of mordant dyes), a brilliant blue can be obtained by the use of Phthalogen K without this aftertreatment.

COLOUR AND FASTNESS PROPERTIES

As a copper complex, Phthalogen Brilliant Blue gives, according to the strength of the printing pastes or the colour yield on the various materials, colours ranging from an intense brilliant blue with a reddish undertone and a greenish overtone to a bright turquoise blue.

By means of Phthalogen K it is now also possible to obtain full reddish blues on viscose rayon.

The nickel dye is considerably greener and gives, in medium and pale prints or pads, attractive, greenish turquoise blues.

The fastness to light and weather of the copper-complex dye is outstanding; whilst that of the nickel complex is not quite so good, but is, nevertheless, still very good. The fastness to washing and boiling of both dyes (5) is outstanding. The fastness to rubbing depends to a certain extent on the careful production of the prints, and under favourable conditions is about 5. An important point is the complete removal of the thickening. Prints available from the trade show a high fastness to rubbing. The fastness to chlorine is 4, and is therefore sufficient for most purposes.

The pigments obtained on the fibre are also remarkably resistant to organic solvents and plasticisers, and withstand the crease-resist and the well known Trubenising processes.

PRINTING ALONGSIDE DYES OF OTHER GROUPS

As illuminating colours printed alongside Phthalogen Brilliant Blue IF3G (copper or nickel complex), the Rapidogen dyes are chiefly used, both the older types developed in acid steam and the new Rapidogen N brands developed in neutral steam being suitable. Phthalogen Brilliant Blue IF3G in roller printing is not affected by tarnishing of the roller, and small quantities of alkaline printing paste taken up by the Phthalogen print from the subsequent Rapidogen printing roller are rendered harmless by the ammonium acetate in the Phthalogen paste. The introduction of alkali into the printing paste may cause noticeable inconvenience, however, when the Phthalogen Brilliant Blue is printed after the Rapidogens. Where it is necessary to print the dyes in this sequence, it is advisable to interpose a water roller between the Rapidogen and the Phthalogen Brilliant Blue. If the Rapidogen portions of the print are small and the Phthalogen portions large, however, the introduction of alkali into the Phthalogen colour will not lead to trouble.

From a chemical point of view, interference with the coupling of the Rapidogen dye by the catalytically active metal of the Phthalogen Brilliant Blue

might be expected to lead to trouble. In actual practice, however, this does not occur.

Although, in view of the above considerations, it appears advisable to print Phthalogen Brilliant Blue first, the method adopted in actual practice, however, is frequently to print the Rapidogen dyes first, to interpose a water roller, and then to print the Phthalogen Brilliant Blue IF3G.

Rapidogen dyes together with the blue and green Phthalogen dyes thus offer an extremely comprehensive range of shades, especially when it is remembered that the Phthalogens (with copper or nickel) can be printed in all depths down to pale shades without noticeable risk of diminishing the fastness properties.

Alcian Blue can also be used simultaneously as a bright, pale turquoise blue.

For paler illuminating colours and shades which cannot be obtained with Rapidogen dyes, the ester salts of the leuco vat dyes (Indigosols, etc.) are suitable. They can be printed by the chlorate or by the nitrite process. In the latter case, a sulphuric acid or sulphuric acid-nitrite bath can be used simultaneously for the development of the Indigosols and the aftertreatment of the Phthalogen dye. As regards the sequence of printing, the same observations apply in this case as were made with respect to the Rapidogen dyes. As a rule, the Indigosols are printed before Phthalogen Brilliant Blue with the interposition of a water roller.

Where, in a pattern, overprints occur, it is advisable to print the Phthalogen Brilliant Blue IF3G first and the Rapidogen or Indigosol dyes last, as this results in more uniform mixed shades than can be obtained in the reverse order.

An inherent characteristic of the bright blue colour of the copper phthalocyanine is that it gives particularly attractive designs alongside black on a pale ground. The question of a suitable black, both as adjacent and as overprinted outlines, is therefore of particular importance. Aniline Black cannot be used for this purpose, as on the one hand development is prevented by the volatile bases from the Phthalogen Brilliant Blue paste, whilst on the other hand the aniline vapours may react with the Phthalogen. In machine printing, a still further difficulty is the influencing of the colours by mutual transfer.

Diphenyl Black behaves much more favourably, but is insufficiently developed where Phthalogen Brilliant Blue is overprinted.

Rapidogen Black is suitable for printing alongside Phthalogen Brilliant Blue, and the neutral process is to be preferred. Either the Phthalogen is printed before the Rapidogen Black or, if the reverse procedure is adopted, a water roller is interposed before the blue. In the latter case, however, the black loses some of its tinctorial strength owing to squeezing. If the Rapidogen Black overprints the Phthalogen Blue portion, the black suffers considerably. A black which remains practically unaffected and can be overprinted is obtained by mixing Rapid Fast Blue BN and Rapid Fast Yellow GH cone.

Indigosol Black also can be used where overprints occur.

Acramin Black is satisfactorily fixed when printed first, but, owing to the subsequent squeezing, the tinctorial strength suffers in multi-coloured roller prints. If the black overprints the blue portions it is insufficiently fixed where it is printed on the Phthalogen Blue. In screen printing, Acramin Black printed first gives a deep black under Phthalogen Brilliant Blue IF3G.

The use of vat dyes as illuminating colours alongside Phthalogen Brilliant Blue IF3G is limited in two directions. (When Phthalogen prints come into contact with vat prints, the two colours exert a mutual influence: i.e. the vat dyes partly prevent the development of the blue in their immediate vicinity, and at the same time the vat print is weaker where it comes into contact with the Phthalogen. In roller printing, this difficulty can be overcome, by interposing a water roller before the Phthalogen print, to such an extent that no noticeable defects are apparent when the colours are adjacent. Where the colours are separated by a space in the pattern, printing difficulties of a technical nature do not occur.

No trouble has been caused by the vat dye components being carried over into the Phthalogen paste. One disadvantage is the change of colour which the blue may undergo on being steamed when it is printed alongside vat dyes. Presumably, the duller colour which results is due to the volatile decomposition products of the Rongalite. We have not been entirely successful in overcoming these difficulties, but it would seem possible to obtain the normal shade of the blue by paying particularly careful attention to the renewal of the steam, so that the troublesome Rongalite decomposition products are continually removed. Owing to the difficulties mentioned, it has been impossible up to the present to introduce Phthalogen Brilliant Blue as a subsidiary dye for printing alongside vat dyes.

Tests carried out in actual practice have shown that Phthalogen Brilliant Blue IF3G can also be printed on naphtholated goods alongside azoic diazo components. The usual ground for base print-on styles is used; in this connection it is best to keep the quantity of caustic soda low and to use no Turkey Red oil product. In the tests mentioned, the impregnation bath contained only a synthetic wetting agent. Setamol WS, a condensation product of naphthalene-2-sulphonic acid and formaldehyde, is suitable as a protective colloid. The diazo component or the azoic composition is printed first, and the Phthalogen can then be printed immediately without a water roller. The Phthalogen printing paste was prepared with Phthalogen K, and differed from the usual printing paste only in the use of a double quantity of ammonium acetate. Prints were also produced with azoic compositions in the reverse order without any adverse effect due to copper being carried over from the Phthalogen printing paste. The aftertreatment consists in steaming, acidifying, stripping the naphthol in alkali, and soaping at the boil.

Many attempts have, of course, been made to include other dyes in the Phthalogen printing paste in order to increase the possibilities of shading,

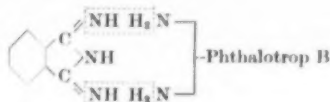
which, in the Phthalogen group itself, are limited to the use of mixtures of metal salts and the combination of the blue with the green dye. Greens can be obtained by mixing Phthalogen Brilliant Blue IF3G (Phthalogen K) with Rapidogen Yellow N-14G, but the printing results obtained in actual practice have not been sufficiently consistent.

THE RESISTING OF PHTHALOGEN BRILLIANT BLUE IF3G

There are various possibilities for the production of resists under Phthalogen Brilliant Blue IF3G. One process may consist in binding the metal, so that condensation to the metal complex cannot take place. A further means is the destruction of the intermediate product, e.g. by strong alkalis. A third method of preventing the formation of the dye on the places to be resisted is the reaction of the Phthalogen intermediate product with substances which have a primary amino group in the molecule. The first process obviously plays a part in a method using tartaric acid as a resisting agent for first-printed resists. In addition to a copper-complexing action, precipitation of the basic Phthalogen intermediate product as a difficultly soluble salt also plays an important part. This method is, unfortunately, less suitable for coloured resists. A further possibility is the preprinting of resists with formic acid and zinc oxide. In this way really good white effects were obtained, but in this case also it was difficult to obtain coloured resists. The use of caustic soda in resists offers the possibility of producing white resists by the first-printed process, and, moreover, vat dyes can be fixed as coloured resists in Rongalite printing paste rendered alkaline with caustic soda. It has, however, proved necessary to incorporate in the paste considerable quantities of solid substances, such as whitening, in order to avoid the formation of halos. These additions, of course, present certain technical disadvantages in printing. Moreover, in resist printing with vat dyes the same difference in the colour of Phthalogen Brilliant Blue is to be expected as was observed in the case of direct printing.

The third method mentioned above was successful. The principle is based on the property of the Phthalogen intermediate product of entering into a relatively smooth reaction with primary amino compounds with the formation of substitution products which can no longer be condensed to the dye and are hydrolysed and washed out during the acid aftertreatment. A compound of this kind has just been marketed under the designation *Phthalotrop B*. It is a basic liquid of fairly high boiling point.

The reaction on which the resist is based may be illustrated by the formula—



The reaction leads, by elimination of ammonia, to substituted products which can no longer be condensed to the dye and which are hydrolysed and washed out by acid aftertreatment.

In principle, Phthalotrop B can be used for both first-printed and overprint resists, although the former method is preferred in practice, because pads of Phthalogen Brilliant Blue, either during drying or after standing for some time, show a partial development of the dye which adversely affects the resists. This premature development can be counteracted, by an addition of Trilon A to the padding liquor, to such an extent that satisfactory overprint resists can be obtained even after the lapse of some time. Such pads must be developed by dry heat at 284°F. (140°C.).

By the first-printed process, absolutely clear, sharply defined white resists are obtained; coloured resists are also possible, both Rapidogen and the more recent Rapidogen N dyes being primarily suitable. The process consists in printing the resists, carefully drying, padding with a solution containing Levasol PO and Phthalogen K and having a pH of about 8, and then drying and developing in steam. As thickening agents we recommend British gum-tragacanth or British gum-starch mixtures. All the previously mentioned precautions must be taken when drying. A partial formation of the dye during the drying is by no means disadvantageous. Depending on the nature of the material, the dried pads assume a more or less greenish colour. The aftertreatment after steaming is the same as for direct prints. In addition to Rapidogen dyes, Rapid Fast and Anthrasol dyes can be used for coloured resists. As a black, without the addition of a resisting agent, the mixture of Rapid Fast dyes already mentioned in connection with direct printing is suitable.

Phthalogen Brilliant Green IFFB

Further research and development have succeeded in isolating and manufacturing on a bulk scale a similarly composed substituted derivative producing a green colour equal to the blue in brilliance and having similar fastness properties.

The process of producing the green pigment on the fibre is, in principle, similar to that for the blue pigment, but details of the manner in which the process is carried out differ somewhat.

THE INTERMEDIATE PRODUCT

Phthalogen Brilliant Green IFFB is marketed as a pale yellowish powder similar in character to Phthalogen Brilliant Blue IF3G. It is a base, and shows good stability when stored in a dry place.

SOLVENT

For the development of the green, a larger quantity of solvent is normally required than for the blue. To keep the costs as low as possible, in addition to Levasol P or PO, the cheaper formamide, marketed as Levasol F, is used. As compared with Levasol P, Levasol PO offers the advantage of less inconvenience due to odour on evaporation.

METALS

The metals for the phthalocyanine dye to be formed are in this case also copper and nickel. Owing to its particular brilliance, the most valuable dye is prepared with copper; only Phthalogen K is recommended in this case, as it shows more reliable

results than copper salts. For the nickel dye, nickel chloride or sulphate can be used.

Attention must also be paid in this case to the maintenance of a definite ratio of metal to intermediate product. The pH of the ready-made printing paste is about 8.5. In the case of the green printing paste, special buffering by means of ammonium acetate is unnecessary.

PRINTING PASTE

This contains 25–30% of solvents in the case of a full print, about 15–20% being Levasol P or PO.

The solubility of Phthalogen Brilliant Green IFFB is not so high as that of Phthalogen Brilliant Blue IF3G. Even in the mixture of solvents containing Phthalogen K solution, complete solution is not obtained. For this reason, a dispersing agent—Emulsifier W—is used. After pasting up with Levasol P or PO, Emulsifier W is added before Levasol F and Phthalogen K solution are incorporated. In this way a partial solution is obtained which holds the undissolved substance in fine suspension. This undissolved portion is used when the dye is developed.

The function of the solvents is the same as in the case of the blue pigment. An increase in the quantity of solvents exerts a favourable influence on the evenness of the prints and the fastness to rubbing, particularly on fabrics made from filament and staple rayon.

The stability of the printing paste is limited, as in the case of the blue, but the cooler it is stored, the better it will keep. The chief reason for the loss of tinctorial strength is, in this case also, the hydrolytic decomposition of the intermediate product. With the green also, the printing paste must be kept in the dark.

Tragacanth and other thickening agents which can be easily washed out are particularly suitable. Further, the products mentioned as being suitable for Phthalogen Brilliant Blue IF3G can be used, either alone or in admixture with tragacanth.

TEXTILES

Regarding the textiles for which Phthalogen Brilliant Green IFFB is suitable, the remarks made in connection with Phthalogen Brilliant Blue IF3G also apply here. On viscose filament and staple rayon the tinctorial strength and brightness are, in general, at least as good as on cotton. On all these fibres the shades obtained are practically the same.

PRINTING AND AFTERTREATMENT

With respect to behaviour during printing, what has been said regarding the blue also holds good in this case. No particular sensitiveness to light was noticed when wet prints were left lying on the screen printing table.

A thorough drying of the prints until the water is completely removed is just as important for the full development of Phthalogen Brilliant Green IFFB as it is in the case of Phthalogen Brilliant Blue IF3G. The guiding principles given under the latter dye are also applicable here.

The condensation to the dye is obtained, as in the case of Phthalogen Brilliant Blue IF3G, by neutral or acid steaming for 5–10 min. When acid steam is

used, any great excess of acid must be avoided. The dry heat treatment is also carried out in condensation apparatus or on cylinders at 275–284°F. (135–140°C.) for 6–8 min. In this case, the higher quantities of solvent (30% for a full shade) are used.

With the green it is also necessary to give an acid aftertreatment to remove the by-products which dull the colour. In addition to sulphuric acid or hydrochloric acid, either formic acid alone or oxalic acid plus formic acid can be used in an almost boiling bath.

COLOUR AND FASTNESS

The dye formed with copper gives greens which it was previously impossible to produce with such good fastness properties on cellulose fibres. The brilliance is particularly remarkable in the medium depth. The fastness to light on cotton and rayon staple (7–8) is outstanding. The fastness to weather is very good. Fastness to boiling soda, fastness to washing at 212°F. (100°C.), and fastness to peroxide are of the highest order. The fastness to chlorine is 4–5. The dye formed with nickel possesses a bluer, considerably duller, shade and also has very good fastness properties.

PRINTING WITH OTHER DYES

As illuminating colours alongside the green, Phthalogen Brilliant Blue IF3G (copper or nickel complex), Rapidogen, Rapid Fast, Anthrasol, and mordant dyes can be used, but the last-named must be sufficiently resistant to the necessary acid treatment and soaping at the boil. For printing alongside vat dyes, the same limitations apply as in the case of Phthalogen Brilliant Blue IF3G, so that the general use of this dye alongside vat dyes is out of the question. Troublesome influences mutually affecting the dyes may be expected when Phthalogen Brilliant Green IFFB is printed alongside Aniline Black, which is therefore suitable only for patterns containing small black portions which are separated from the green parts of the design.

In the case of multicoloured machine prints it may, under certain circumstances, be advisable to

interpose a water roller before the green printing paste.

Phthalogen Brilliant Green IFFB can be combined in the printing paste with Phthalogen Brilliant Blue IF3G to produce intermediate shades. In particular, mixtures of the two copper dyes give beautiful, bright turquoise blues to bluish greens.

PADDING AND RESISTING

In principle, the padding and the resisting of Phthalogen Brilliant Green IFFB are possible. The production of suitable padding solutions requires a high concentration of acetic acid, so that the process can be carried out only on apparatus which is resistant to acid. Careful attention must also be paid to good ventilation.

Phthalogen Blue IB

This most recent addition to the Phthalogen range differs from the Phthalogen Brilliant Blue and Green products in respect of both chemical constitution and recipe for application. The yellowish-brown product already contains the metal atom cobalt, and is applied under acid conditions together with a reducing agent, quinol, which is marketed under the designation Levasol R powder.

The colour value of this blue is very high, so that the new product is suitable for the production of bloomy navy blues. It has outstanding fastness to light, good fastness to boiling, but poor fastness to chlorine.

* * *

The author wishes to express his thanks to the Directors of Farbenfabriken Bayer for permission to give this lecture; to the inventors Dr. F. Baumann, Dr. B. Bienert, Dr. G. Rösch, Dr. H. Vollmann, and Dr. W. Wolf for their interest and advice; and to Herr H. Barth for his co-operation in the practical work.

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GERMANY

(MS. received 2nd March 1953)

Reference

¹ Gund, F., *Melliand Textilber.*, **31**, 46 (1950).

Discussion

Dr. T. VICKERSTAFF: In view of the small molecular size of the phthalocyanine precursor, have the phthalogen products any advantages when applied to the newer synthetic fibres?

Dr. F. GUND: Trials were made on polyamide and polyacrylonitrile (Orlon) types of fibre, but fixation, yield, and shades were not satisfactory. It seems that the ingredients do not penetrate equally into the fibre, and that therefore the dye cannot be properly formed inside the fibre, but only on the surface.

Dr. E. KRÄHENBÜHL: Has the lecturer tried to apply the phthalocyanines to synthetic fibres by a technique similar to the cuprous ion method for dyeing acrylic fibres, which, as is known, absorb also prior to dyeing appreciable amounts of copper. This would also apply to wool. By this mordanting process and subsequent introduction of the phthalogen compound, the bulky complex could possibly be formed within these fibres.

Dr. GUND: The application of copper prior to dyeing was tried without success. The low stability of the phthalogen preproduct would not allow its subsequent application on synthetic fibres from an aqueous bath at elevated temperatures.

Mr. A. S. FERN: What proportion of the linear "polymer" is formed, under general printworks practice, when Phthalogen Brilliant Blue IF3G is "polymerised" in presence of copper? What factors cause this proportion to increase? Is the amount of linear condensate greater or less in the case of Phthalogen Brilliant Green IFFB?

Dr. GUND: An exact determination of this proportion was not carried out. We estimate that, when copper chloride is used, no more than about 10–20% of by-products are formed, depending on drying conditions. Insufficient drying increases the proportion of by-products. When Phthalogen K (copper complex) is used, the tendency to form linear condensates seems to be lower, as shown by

the brilliancy of shade before acid treatment. The tendency to form linear by-products seems to be less in the case of Phthalogen Brilliant Green IFFB.

Mr. F. V. DAVIS: Can Dr. Gund say whether any extension in the range of colours is contemplated? What is the possibility of obtaining a wide range of shades—violets, reds, etc.?

Dr. GUND: An extension of the range can be expected within certain limits only. There is scope for obtaining redder blues than IF3G, but it is unlikely that violets or reds of high fastness properties can be produced.

Mr. DAVIS: Has any value been found in metal complexes other than copper and nickel?

Dr. GUND: Metal complexes other than those with copper and nickel and, of course, cobalt also, were investigated, but either the shades or the fastness properties were found of little value compared with the copper and nickel phthalocyanines.

Mr. DAVIS: Would Dr. Gund elaborate on the critical nature of drying? What does he regard as the ideal drying method?

Dr. GUND: Drying of paddings is, of course, more critical than drying of prints. For the latter the usual can drying method is suitable, provided that complete removal of moisture is achieved. For paddings the hotflue-drying method was found best, but also on hot air jet drying equipment even results were obtained. Equal distribution of airflow is important to prevent any unevenness by migration. Can drying works satisfactorily on even fabrics, but there is a tendency to exaggerate any weaving faults. Therefore, it is necessary to modify the equipment either by wrapping one or two pairs of cans at the start of the range, or to install an air-dryer, e.g. Spooner unit, in front of the can range. After having passed this Spooner unit, the moisture content of the fabric will be lowered to such an extent that no migration takes place on subsequent can drying.

Mr. DAVIS: Perhaps Dr. Gund would say more on the effect of temperature on storage life of printing colours. We have ourselves kept printing colours in a refrigerator for a week or more with little or no loss of colour value, but in a hot room, colour value falls off in a few hours.

Dr. GUND: Regarding the dependence of the rate of hydrolysis of the phthalogen upon temperature (see Fig. 2), it is obvious that storage at low temperature distinctly increases the life of printing colours or pad liquors, and it is most interesting to learn from Mr. Davis that this behaviour was confirmed in bulk work.

Mr. J. W. DUARTE: With reference to Mr. F. V. Davis' question concerning the possible usefulness of phthalocyanines containing metals other than those in common use, I have always understood that this question was investigated fairly early in the history of phthalocyanines. As I

understand it, the stability of a metal phthalocyanine depends upon the closeness of fit of the co-ordinated metal atom in the "hole" in the centre of the phthalocyanine molecule. Metals which are markedly too small or too large for a close fit in this "hole" give phthalocyanines which are unstable, e.g. to acids, whilst those in common use, such as copper, fit closely. Can Dr. Gund inform us whether this view is still held?

Dr. GUND: I have not heard of any new theoretical view on this question. Apart from the closeness of fit the characteristics of the bond-forming electrons in the metal atom also seem to be involved in the stability of metal phthalocyanines.

Dr. W. SHAW: The use of the phthalogen dyes in practice is restricted to some extent by the lack of suitable dyes, especially yellows, for shading purposes. Have any further advances been made towards solving this problem?

Dr. GUND: Further trials have been carried out in relation to the use of mixtures of Rapidogen Yellow and Phthalogen Brilliant Blue, but unfortunately no further success has been achieved in this field. We can report, however, that some trials have been made with combined prints using vat dyes in the Phthalogen Brilliant Blue paste, and developing by "curing" followed by pad-steaming (colloresin process). These results are now having their fastness properties tested.

Mr. D. A. DERRETT-SMITH: Have any experiments been made in mixing yellow vat dyes with either blue or green Phthalogens to give yellow-green shades? If so, are these mixtures subject to the same abnormal fading often shown by a mixture of blue or green vat dyes with yellow vat dyes?

Dr. GUND: Experiments in mixing vat yellows with phthalogen have been made in the way already mentioned. Exposures to light of such prints have just been started, and nothing can be said about their fastness to light.

Mr. R. THORNTON: Dr. Gund indicates in his paper that more difficulty is likely to be encountered with viscose staple fibre than with cotton, which view falls into line with normal experience of phthalocyanine derivatives. Is anything known of the mechanism of coloration, and has the advent of Phthalogen K made this picture any clearer?

Dr. GUND: Empirical data in conjunction with knowledge of the characteristics of the components involved may give an idea of the mechanism of coloration. As mentioned in the written paper, an intermediate copper complex of the Phthalogen pre-product is formed when copper salts are used in the printing paste. Obviously this complex does not diffuse into viscose rayon at the same rate as the other ingredients. When using Phthalogen K no such complex can be formed, since Phthalogen K itself is a relatively stable copper complex. The original products present in the printing paste seem to diffuse more uniformly into the viscose rayon, so that, finally, the conditions for the production of the pigment in good yield are obtained.

Observations on Textile Printing in the U.S.A.

OTTO HABEL

Textile printing in the U.S.A. is discussed with particular emphasis on the more recent developments. The paper deals in the main with machine and screen printing, but passing reference is made to hand block and spray printing.

MACHINE PRINTING

Although the fundamental principles of Bell's original invention of 1783 are still followed, many changes have resulted from a desire to improve the mechanism of printing itself from the standpoints of increased productive capacity and of greater feasibility of fabric styling. More recently many changes have been necessitated by the availability of both new dye classes and new fibres. One of the most important improvements has been the use of the separate back rig drive instead of the former drive from the printing rollers through the printing drum and thence to the dry cans and other back rigging. In this respect print quality has been improved by allowing goods to be printed with less pressure on the print rollers. Through the invention of the synchronous drive, improvement and control of fabric tension were obtained. Fabric tension has been further controlled by the use of a J box to feed the goods to the printing machine instead of the customary roll, which at the same time allows new yardage to be sewed on without stopping the printing machine. A survey reveals that change continues to characterise current textile-printing practice.

Emphasis is being placed on developing higher-speed printing machines, but there are factors which limit further increases in speed. At higher speeds the inevitable problem of foaming in the colour box presents itself. Through the use of an intermediate furnishing roller, driven at a speed differential, and allowing slower rotation of the colour-box furnisher, foaming has been controlled in machines running at high speeds.

Another limiting factor has been the use of the inefficient steam cans for the drying of prints. Although they are satisfactory on dry days, the printer finds it necessary to run them much more slowly on humid days in order to dry the prints thoroughly. Various aids such as hot-air blowers have been used to decrease the drying time on the cans on humid days. Although at present having very limited use, the wider application of hot-air, oven-type dryers may be predicted, which would allow an accurate design for the capacity desired, maintaining constant speed regardless of the ambient relative humidity.

Of primary importance to the modern printworks is its ability to decrease "down time". Through the use of hydraulic forcing jacks to speed the changing of mandrels, and by having spare colour boxes, furnishers, mandrels, doctor blades, and rollers, the time involved in changing over patterns may be held to a minimum. Along these same lines the J box feed, the endless backgreys with continuous washing and drying facilities, as well as a spray for

moistening print cloth, ensuring better penetration—all have been helpful in keeping the machine running.

Improvements in the colour brightness of printed fabrics have been made possible primarily through the use of lower pressures on the print rollers, which thus overcomes the "bloom-killing" effect due to the crush of the rollers. The use of lower pressures on the printing rollers has decreased the arc of contact, which in turn has resulted in increased sharpness of outline of printed objects. The newer printing machines have been designed to ensure a smaller arc of contact by adopting a separate pressure roller for every print roller.

Although plastic film is being printed to-day on machines very similar to those printing textile fibres, several differences in design should be noted. In view of the lack of absorbency of the material being printed, the machine is designed to allow a much greater space between rollers applying successive colours. This factor alone has limited the capacity of these machines to four to six colours. Although very few plastics printers are using backgreys at present, more widespread use of greys may be expected, if only to protect the rubber printing-machine blankets from the solvents contained in the pigment inks. Long printing-machine blankets are most satisfactory, in that they allow greater time for continuous washing and drying, which is necessary because of the nature of the inks printed. Through the use of raised engravings instead of the common intaglio engravings, the quality of the prints may be improved. Because the decoration of polyvinyl chloride film is strictly a surface application, the raised engravings do not allow the succeeding rollers to touch the print. In this case the spacing between the rollers is not so important.

The great majority of textile printworks to-day are essentially high-production units. Perhaps more than in any other country, the keynote in practically every plant in the U.S.A. and throughout each separate operation is "production". High wage scales force the printer to produce prints of the necessary quality in minimum time. These high wage scales motivate our efforts to increase production not only through improvements in mechanisms, dye technology, and new fibres, but also through styling. Many patterns are simplified so as to eliminate intricate details that might slow down production. Those processes which require many hours of painstaking effort, for that reason, will continue to be done in Europe more extensively than in the U.S.A. Among such processes that come to mind especially are various resist styles. While fast-colour resist prints were not possible in the early years of textile printing, we find that to-day

white and coloured resists in a wide range of colours and dyed grounds can be produced conforming to the highest fastness standards. When extended to include conversion effects resulting from overlapping prints of distinctly different dye groups, the technique of resist printing can be justly considered one of the most intricate yet fascinating in all textile printing. Resist printing gives free rein to the ingenuity of both designer and printer in obtaining print effects unobtainable by any other means. Such styles, the cost of which is often prohibitive in the U.S.A., are carried out only on a limited scale even under favourable conditions. While the emphasis in America is on production, American methods demand emphasis also on quality at the same time. On the other hand, if quality beyond that necessary is sought after, the effort is wasted and costs and production rates may suffer.

PIGMENT PRINTING

The period just prior to and following World War II witnessed the introduction of a variety of new printing methods of varying degrees of significance. From the standpoint of practical value and the degree to which it has been adopted by the printing trade, the pigment-printing principle is by far the most important. Until the development of the modern technique by the Aridye Corporation, pigment-printing had fallen into almost complete disuse. One finds today only rarely a machine printer in the United States who does not make use of pigment colours marketed under such names as Aridye, Sherdye, Suntone, and Aulabrite.

The Aridye pigment colours consist principally of highly concentrated pigment-colour dispersions in an organic-solvent solution of a synthetic resin. As these colour concentrates also contain emulsified water, they can be considered as water-in-oil emulsions which are miscible with organic solvents; addition of water increases their viscosity. Print pastes are prepared by diluting a colour concentrate with a colour-free oil-in-water emulsion, which is called a "clear". The clear is prepared by adding an organic solvent to a synthetic resin containing "clear concentrate" and further adding water while "homomixing" with an Eppenbach Homomixer. The colour concentrate is mixed with this emulsion in the desired proportions.

Colourists usually sum up the main advantages obtained by the use of such pigment colours as follows—

- (1) The printer is able to observe any irregularities during printing, since the colours are visible
- (2) Uniform prints are obtained no matter how light the shade
- (3) Suitability for printing alongside other dye groups
- (4) Brightness of colour combined with good light fastness.

While the fastness to rubbing of such pigments is generally considered satisfactory for a variety of end uses on a variety of fabrics, they are not used indiscriminately where the utmost fastness to rubbing and abrasion is desired. One finds more recently that small additions of synthetic rubber emulsions are being made to print pastes, prepared as outlined, in an effort to improve further the

fastness to rubbing, particularly in the case of dark shades.

During the past three or four years a water-miscible oil-in-water emulsion has been marketed by Aula Chemicals Inc. under the name of *Aulabrite*. Aulabrite colours are concentrated pigmented resin emulsions, which are mixed for printing purposes with Aulabrite clear extenders. Since the Aulabrite extenders also are oil-in-water emulsions, the final print pastes are miscible with water. The new system shows the following advantages in addition to those of pigment printing in general—(i) equipment, mixing tanks, rollers, brush rollers, and screens can be washed readily with water; (ii) print pastes are stable and permit high machine speeds; (iii) these colours may be washed with ease from rubber blankets and backgreys, whether continuous or not; (iv) in spite of the water-miscible nature of the print pastes before printing, the prints are very fast to laundering and dry cleaning, and show excellent rubbing fastness. To do justice to this subject would require separate treatment.

PHOTOGRAPHIC PRINTING

The production of photographic images on sensitised textile fabrics, although not directly related to textile printing, deserves mention as another mode of colouring fabrics, which achieves effects somewhat similar to those produced with photo-engraved rollers. The principal process employed at present is based on the fact that certain leuco vat esters (Algosols or Indigosols) can be developed into the coloured pigment of the parent vat dye by exposure to light. Light develops the sensitised surface of a photographic image, and hence the copying process has to be done with the aid of a photographic negative. In practice this is accomplished by the use of a special copying machine composed essentially of a Plexiglass cylinder, over the perimeter of which is attached the photographic negative, and in which a high-pressure mercury-vapour lamp emits ultraviolet rays. Passage of Algosol-sensitised fabric over the cylinder causes colour development in exposed negative areas. The undeveloped Algosol is stripped off the sensitised textile surface by means of a hot bath of sodium silicate. This process enjoys some popularity for dress goods.

VAT-DYE PRINTING

In keeping with the desire to make the print plant more efficient and consequently more productive, printing speeds have been accelerated in recent years to a point where a speed of 120 yd./min. or higher is not considered exceptional. The ability to maintain or even approach this rate of production in subsequent print processing, viz. aging, soaping, etc., is considerably restricted in the case of vat dyes because of the 7- to 10-minute aging usually required for accomplishing the following principal phases of colour fixation—

- (1) Dissolution of the active ingredients, viz. Rongalite, potash, etc.
- (2) Reduction of the vat pigment to its leuco form
- (3) Absorption of the available leuco vat dye by the fibre.

Flash Method

Although attempts along conventional lines to reduce fixation time materially have not met with success, it is interesting to note that satisfactory vat-dye fixation has been obtained within 30 sec. by a number of screen printers using the "flash method". This method consists essentially in printing the vat dye without the addition of hygroscopic agents, such as glycerol or the usual reduction components, and in using either Cellapret DKN (a methyl cellulose compound) or locust-bean gum along with a small amount of starch as a thickening. In other words, the vat dye is printed as a pigment. The prints, after being dried, are padded with caustic soda and hydrosulphite, and, without intermediate drying, are steamed for approx. 20 sec. at 230–240°F. They are finally oxidised and washed. Coagulation of the thickenings of the paste when brought into contact with alkali prevents marking-off during the chemical padding. The absence of glycerol from the print paste facilitates complete drying, and the omission of reducing agent gives prints an unlimited stability. The fact that unsteamed prints do not undergo any change has helped considerably to increase the popularity of this process for printing drapery fabrics. A modification of this principle is also employed in screen printing, whereby the dried print is padded with Rongalite (sodium formaldehyde-sulphoxylate), potassium carbonate, and glycerol instead of hydrosulphite and caustic soda, and, without intermediate drying, is aged at 230°F. for 5–7 min. in a tower ager. That prints prior to printing may be stored for any length of time is an obvious feature of this process.

There appears to be an increasing interest in the U.S.A. in utilising the chemical-pad process in machine printing, and some very promising pilot-plant prints indicate that, by the use of this method, a substantial reduction of the actual steaming time is possible. Needless to say, the part played by the print thickener in the diffusion of the leuco vat dye into the fibre during a shorter aging period is very important. For instance, thickeners containing relatively high amounts of solid tend to obstruct the transfer of the leuco vat dye to the fibre substance.

The above features and the fact that the flash method is not restricted to the use of specially standardised printing brands should make the chemical-pad principle of applying vat dyes a valuable adjunct to present-day printing methods.

It is interesting to note that satisfactory vat-dye prints on silk are being produced by the pad-steam flash method without any injurious effect on the silk.

SYNTHETIC FIBRES

With the invention of the various new synthetic fibres, such as Orlon (acrylic fiber), Terylene (polyester fiber), dynel, and others, presenting the colourist with ever new and challenging problems, the technique of the modern textile printworks no doubt will be further greatly influenced. The definitely hydrophobic properties of the newer synthetic fibres, representing extreme difficulties in

satisfactorily printing these structures, are responsible for their limited use in printing. Studies are constantly being conducted to enable the printer to handle such fabrics.

The printing of nylon, on the other hand, continues to be successfully effected with selected acid and direct cotton dyes, as well as disperse dyes and also pigments.

The printer has always encountered difficulties also in printing rayon-staple fabrics. These constructions do not allow prints to be dried, without forming a hard film often injurious to the fibre. While this may be controlled to some degree by carefully regulating drying conditions, we have found more recently that soft gums offered for the printing of sheer fabrics allow satisfactory printing and can drying without trouble.

SCREEN PRINTING

The photographic screen more than any other single factor has considerably widened the scope of and extended the market for silk-screen work. New methods and new procedures are constantly being tried in order to improve further the reproduction of photographic images on textile fabrics.

As far as new developments in colour application are concerned, the "flash method", as discussed earlier, introduced a very satisfactory technique for the screen printing of vat dyes, which allowed the logical choice for prints of best all-round fastness properties. Until the introduction of this new technique, vat dyes found very little use in screen printing.

Attempts are constantly being made to mechanise the screen-printing operation partly or completely, so as to enable the screen printer to handle roller-machine quantities without the initial capital outlay for a roller machine and without the expense of engraving copper shells and chromium plating. Several types of machines are at present in use. The machine finding widest acceptance in the U.S.A. is imported from Switzerland and operates on the principle of having the fabric, previously combined with a suitable rubber sheet, moved forward on an endless belt and then printed by a series of screens arranged one next to the other along the belt. The screens are raised and lowered automatically, and are provided with squeegees which can be set to give a variable number of strokes. At the end of the printing operation the goods are automatically removed from the belt and passed through a drying chamber. The belt is washed and dried automatically.

BLOCK AND SPRAY PRINTING

Hand-block and spray printing are practised on a very limited scale. Block printing has almost become a lost art, while spray printing in recent years has found some application, particularly in the printing of men's neckwear.

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Discussion

Mr. W. J. MARSHALL: The rate of reduction of vat dyes at around 100°C. is of the order of 30 to 60 times that at room temperature. In view of this, there would seem little point in having an air passage of 15–20 seconds between the padding process and the steaming, particularly so, as there will also be considerable loss of hydrosulphite and alkali. In the normal leuco-pad-steam process the gap between padding and steaming is kept to a minimum, in many cases corresponding to a fraction of a second in passage time. Since this air passage cannot contribute appreciably to the reduction, what is the true reason for requiring an air passage as great as approximately 18 yards? In the "flash reduction" method of developing vat prints is the "caustic-hydrosulphite" padded hot? The reason this question is asked because you say that in many cases a considerable amount of reduction occurs in the 15 to 20 seconds before the cloth enters the steamer.

Mr. O. HABEL: Tests have shown that not more than 15 seconds must elapse between the padding and the steaming, in view of the fact that there is of course, a loss of hydrosulphite. The loss of hydrosulphite, however, does not reflect itself in a poor colour yield, particularly with heavier fabrics, due to the considerable pickup during the padding. It is the opinion of the speaker, however, that the air passage is best kept at a minimum. Newer constructions of flash agers, do not allow the air passage referred to, bringing the opening of the ager close to the paddler.

The caustic and hydrosulphite padding liquor is kept at room temperature.

Dr. E. KRÄHENBÜHL: Will the lecturer tell us what is the normal temperature in the flash ager?

Mr. HABEL: The temperature in the flash ager, for best results, is kept close to 230°F.

Dr. KRÄHENBÜHL: In my experience a mixture of wheat starch and locust-bean gum gives better results than locust-bean gum alone. Not only must the dye be prevented to flush out of the thickening, but the chemicals coming from outside must also be enabled to penetrate the film of thickening which obviously becomes more porous by the addition of starch and results in a better colour yield.

Mr. HABEL: Mixtures of starch and locust bean gum no doubt are very good. Printers in many cases, however, favour mixtures with alginates, due to difficulties in removing the starch during the soaping operation in order to obtain crock-free prints.

Mr. J. MITCHELL: In view of the trouble experienced by marking off at the padding mangle during the treatment of prints by the "flash" method, has the application of Formosul and alkali been tried by spray methods. If this were possible it would obviate the marking off trouble and save applying excess of liquid?

I am sorry that I did not catch the figures relating to production by a roller and a screen plant operating in the U.S.A.

Mr. HABEL: The application of Formosul and alkali by spraying also has been tried to obviate marking off and save applying excess of liquid. The control of such a spray for different patterns and different fabrics, however, is a difficult one.

As to production figures, the speaker found a daily production of approximately 1,500,000 yards on 33 printing machines, an outstanding example. In screen printing, a monthly production of 200,000 yards for tablecloth purposes on 8, 60-yard tables, printing 46 hours a week, is perhaps the most outstanding example achieved in screen printing.

Mr. R. L. HILL: Surely with such high printing speeds, the amount of "D. & K." due to printing faults must be rather high?

If this is not the case, what special precautions do you take to obviate the normal causes of such faults? Do you have special equipment for "getting up" doctor blades, cloth preparation for printing and particularly for ensuring and maintaining grit-free, homogeneous print pastes in the large quantities required?

Mr. HABEL: Chromium-plated rollers are used exclusively, which to some extent helps to eliminate doctor streaks.

Only customary precautions are taken, which do not differ markedly from those taken in other countries.

Mr. J. W. RUWHOF: It is well known in practice, and Saville (*American Dyestuff Reporter*, 1953, p. 272) also mentions it, that the colour efficiency due to the coagulation of the thickener is low sometimes. What is the experience of the author with it?

Mr. HABEL: While it is true that due to coagulation of the thickener the colour yield may be lowered, it must be said that the coagulation with locust-bean gum employed in the U.S.A., is not very marked and therefore does not express itself in objectionable colour loss.

Mr. RUWHOF: There is a lot of argument about O/W and W/O emulsions. It is true, that O/W emulsions give a much better cleaning, but manufacturers of the W/O type claim a much better definition of the print. Which type is preferred in practice?

Mr. HABEL: While water-in-oil emulsion-type pigments are being printed most extensively, I am not in a position to say whether the W/O type gives a better definition than the O/W type.

Dr. T. VICKERSTAFF: The speaker referred to the use of nylon staple continuous back-greys (or printing blankets?). I should like to know whether the use of nylon staple in this connection gives rise to any trouble with "pilling" and if not, how this trouble is avoided.

Mr. HABEL: Spun nylon greys are preferred to the filament type but, of course, do not lend themselves for the printing of every pattern, or every fabric construction, or every engraving. Not widely enough used, I am not in a position to comment on trouble with pilling.

Mr. H. WILSON: Could the speaker give a little more information on the methods employed in

continuous production of thickenings and the method adopted in the control of viscosities?

Mr. HABEL: The method appears to work satisfactorily, the bursting of the starches or gums seems effective, and the subsequent working properties appear to be quite satisfactory.

Mr. W. PENN: The lecturer lists the advantages of the pigment printing processes, but makes no reference to their effect on the handle of the finished material. Can he state to what extent pigment printing is limited in its application as a result of its effect on handle?

Mr. HABEL: I do not believe that pigment printing is limited to any appreciable extent in its application as a result of its effect on handle.

Mr. R. L. DERRY: In his description of the flash reduction method for the fixation of vat dye prints the author said that it was usual for a period of approximately 15 seconds to elapse between the cloth leaving the padding mangle and entering the steamer. Sodium hydrosulphite in alkaline solution is rapidly oxidised in the air and one would expect the traverse of the cloth between the machines to be as short as possible. Is there any special reason for this long interval?

Mr. HABEL: Although sodium hydrosulphite in alkaline solution is oxidised in the air, it does not express itself in lower colour yield since this process is employed mainly for heavier construction of fabrics where the pickup in most cases is such that a slight degradation of the hydrosulphite shows no particular ill effect. There is, however, no special reason for any extended interval between padding and steaming, and in my opinion it should be as short as possible.

Mr. DERRY: How is the locust-bean gum modified before use in this process and is the modification carried out in order to facilitate removal of the gum in subsequent washing off

processes and so avoid the harsh handle which is sometimes imparted to rayon fabrics by this thickening when incompletely removed?

Mr. HABEL: Mixtures of locust-bean gum with alginates are made to facilitate removal of the gum in subsequent washing.

Mr. R. THORNTON: With regard to the previous remarks of Mr. Marshall and Mr. Derry regarding the rate of decomposition of hydrosulphite in the presence of caustic soda, it should perhaps be remembered that in the "flash" vat printing process a pad mangle with a low expression or an engraved pad roller is used. Therefore theoretical considerations regarding hydrosulphite degradation tend to be pointless in view of the vast excess applied to the fabric. This would appear to be a case where the producer prefers to waste hydrosulphite rather than steam and where considerations of production outweigh other items such as drug costs.

Mr. HABEL: It is my experience that the short time elapsing between padding and aging, during which a slight degradation of hydrosulphite is possible, has not expressed itself in poor print results. It is due to the fact that the process generally has been applied on heavier fabrics where the pick-up during padding has been in excess of that necessary for proper reduction. It is my opinion, however, that the air passage is best kept at a minimum.

Mr. N. E. KATRAK: Will you please explain what you mean by: "the endless back-greys with continuous washing and drying facilities"?

Mr. HABEL: An attempt to reduce printing costs resulted in the development of a back-grey washer to provide continuous washing and drying of high quality endless back-grey. The construction of this equipment varies in individual cases.

In closing the Symposium, Mr. F. L. Goodall (*President of the Society*) said that those who had attended the Symposium would return to their daily work stimulated by the papers and discussions and encouraged by personal contact with other workers in their own field. He offered the sincere thanks of those attending the Symposium and of the Council to everybody who had played such a worthy part in making the function the success which it had undoubtedly been.

